HOTOCHEMICAL TRANSFORMATIONS OF A FEW DIBENZOBARRELENES, ENEHYDRAZINE DIONES AND 2(3H)-FURANONES

A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of

DOCTOR OF PHILOSOPHY

by

S. PRATHAPAN

to the

DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY, KANPUR

NOVEMBER, 1987

Dedicated to

My Parents

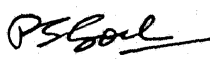DEPARTMENT OF CHEMISTRY

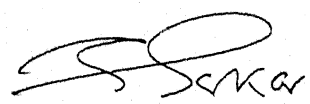INDIAN INSTITUTE OF TECHNOLOGY, KANPUR

CERTIFICATE OF COURSE WORK

This is to certify that Mr. S. Prathapan has satisfactoril completed all the courses required for the Ph. D. programme. These courses include :

Chm 500   Basic Course in Mathematics

Chm 502   Advanced Organic Chemistry II

Chm 511   Physical Organic Chemistry

Chm 524   Modern Physical Methods in Chemistry

Chm 614   Organic Photochemistry

Chm 800   General Seminar

Chm 801   Special Seminar

Chm 900   Post-Graduate Research

Mr. S. Prathapan has successfully completed his Ph. D. Qualifying Examination in February, 1983.

(P. S. Goel)
Head,
Department of Chemistry
I.I.T., Kanpur

(S. Sarkar)
Convener,
Departmental Post-Graduate
Committee,
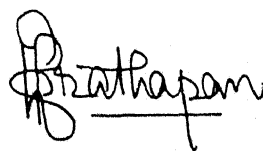Department of Chemistry,
I.I.T., Kanpur.
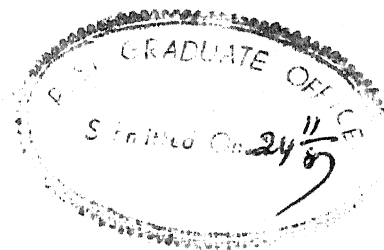
CERTIFICATE II

Certified that the work embodied in this thesis
entitled : "PHOTOCHEMICAL TRANSFORMATIONS OF A FEW DIBENZO-
BARRELENES, ENEHYDRAZINE DIONES AND 2(3H)-FURANONES" has
been carried out by Mr. S. Prathapan, under my supervision
and the same has not been submitted elsewhere for a degree.

M. V. George
Thesis Supervisor

STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, India, under the supervision of Professor M. V. George.

In keeping with the general practice of reporting scientifi observations, due acknowledgement has been made wherever the wor described is based on the findings of other investigators.

S. Prathapan

ACKNOWLEDGEMENTS

It is with pleasure that I thank Professor M. V. George for suggesting the research problem and encouraging me to a successful completion of this work. Also, I wish to express my thanks to Dr. P. K. Das, Radiation Laboratory, University of Notre Dame, for carrying out the laser flash photolysis, fluorescence and pulse radiolysis studies, reported in this thesis.

My thanks are also due to Professor P. S. Goel, Professor S. Chandrasekaran and other members of the Chemistry Faculty, for their encouragement. Of a number of friends and colleagues who have helped me, mention may be made of Drs. P. M. Scaria, C. V. Kumar, M. Muneer, Messrs. D. Ramaiah, H. K. Sinha, R. Manoharan, V. K. Sankaranarayanan, P. Vineetkumar, Paulson John, Prakash Mathews and P. J. Sajan. In particular, I would like to thank Dr. K. R. Gopidas and Dr. K. Ashok for all the help they rendered to me.

My thanks are also due to Mr. B. L. Shyamal, Mr. N. Ahmed, Mr. K. Rajagopalan and other staff of the Chemistry Department for their help and assistance. I wish to thank Mr. C. M. Abraham for typing this thesis, Mr. R. K. Bajpai for drawings and Mr. Mumtaz Ahmed for binding.

Financial assistance from the authorities of Indian Institute of Technology, Kanpur in the form of a Senior Research Fellowship is gratefully acknowledged.

Finally, I wish to express my deep sense of gratitude to my parents, uncle, aunt and brother for their constant help and encouragement.

Kanpur,   S. Prathapan
November, 1987

CONTENTS

PREFACE

The thesis entitled: "Photochemical Transformations
of a Few Dibenzobarrelenes, Enehydrazine Diones and
2(3H)-Furanones" is divided into three chapters.

Chapter I of the thesis deals with our studies on the
photochemical transformations of a few bridgehead-substituted
dibenzobarrelenes such as 11,12-dibenzoyl-9,10-dihydro-9-hy-
droxymethyl-9,10-ethenoanthracene (4f), 11,12-dibenzoyl-
9,10-dihydro-9-ethyl-9,10-ethenoanthracene (4g), 9-benzyl-
11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracene (4h),
9-cyclopentyl-11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthra-
cene (4i), 11,12-dibenzoyl-9,10-dihydro-9-isopropyl-9,10-ethe-
noanthracene (4j), 9-cyclohexyl-11,12-dibenzoyl-9,10-dihydro-
9,10-ethenoanthracene (4k), and 9-cycloheptyl-11,12-dibenzoyl-
9,10-dihydro-9,10-ethenoanthracene (4l).

Irradiation of dibenzobarrelenes 4f-h in solvents such
as benzene, methanol and acetone gave the corresponding
4b-substituted semibullvalenes 5f,g or products such as 11g
and 12h derived from the 8b-substituted semibullvalenes 6g,h.
However, the irradiation of 4j-l gave the corresponding di-
benzocyclooctatetraenes 16j-l, exclusively. The dibenzo-
barrelene 4i, upon irradiation, gave the semibullvalene 5i

and the cyclooctatetraene 16i, in comparable yields.
Reasonable mechanisms have been suggested for the formation
of the various products.

Laser flash photolysis studies of the dibenzobarrelenes
4f-k have shown that the triplets of these barrelenes are
formed in high yields. The reluctance of the barrelenes
4j-l to undergo triplet-mediated rearrangement to semi-
bullvalenes may be related to competing pathways of triplet
decay. The laser flash photolysis studies of some related
barrelenes 4a-e, have also been carried out.

Our findings on the phototransformations of a few ene-
hydrazine diones are presented in Chapter II. The enehydra-
zine diones that we have examined include, (E)-1-(2-benzyli-
dene-1-phenylhydrazinyl)-1,2-dibenzoylethylene (12a),
(E)-1-(2-p-methylbenzylidene-1-phenylhydrazinyl)-1,2-diben-
zoylethylene (12b), (E)-1-(2-p-methoxybenzylidene-1-phenyl-
hydrazinyl)-1,2-dibenzoylethylene (12c), (E)-1-(2-p-cyano-
benzylidene-1-phenylhydrazinyl)-1,2-dibenzoylethylene (12d),
(E)-1-(2-p-acetoxybenzylidene-1-phenylhydrazinyl)-1,2-di-
benzoylethylene (12e), (E)-1-(2-p-carbomethoxybenzylidene-
1-phenylhydrazinyl)-1,2-dibenzoylethylene (12f), (E)-1-(2-p-di
methylaminobenzylidene-1-phenylhydrazinyl)-1,2-dibenzoylethy-
lene (12g), and (E)-1-(2-p-chlorobenzylidene-1-phenylhydraziny

1,2-dibenzoylethylene (12h). These substrates, on irradia-
tion, gave the corresponding pyrazoles 18a-h, and small
amounts of 1-anilino-1,2-dibenzoylethylene (19). On the
basis of UV and ^{1}H NMR spectral studies, we have shown that
E-Z isomerization occurs in the course of the irradiation
of 12a-h. Reasonable mechanisms have been suggested for the
formation of different products from 12a-h.

Transient absorption spectral changes, upon laser exci-
tation of 12a-h, are explained in terms of the formation of
zwitterionic intermediates and, in part, by E-Z isomeriza-
tion. The triplets of 12a-h are short lived and elusive.

Chapter III of the thesis deals with our investigations
on the phototransformations of a few 2(3H)-furanones such as
3,3-diphenyl-5-(4-methylphenyl)-2(3H)-furanone (5b), 3,3-di-
phenyl-5-(4-ethylphenyl)-2(3H)-furanone (5c), 3,3-diphenyl-
5-(4-methoxyphenyl)-2(3H)-furanone (5d), 3,3-diphenyl-
5-(4-ethoxyphenyl)-2(3H)-furanone (5e), 5-(4-chlorophenyl)-
3,3-diphenyl-2(3H)-furanone (5f), 5-(4-cyanophenyl)-3,3-di-
phenyl-2(3H)-furanone (5g), and 5-(4-biphenylyl)-3,3-di-
phenyl-2(3H)-furanone (5h). The major reaction observed
under direct photoexcitation of 5b-h was decarbonylation
leading to the corresponding 1-aryl-3,3-diphenylprop-2-en-
1-ones 6b-h. In contrast, the sensitized irradiation of

5b-h resulted in the formation of 2(5H)-furanones 7b-h, arising through a C-3 to C-4 phenyl group migration. In addition, phenanthrofuranones 9b-h and dimeric products 11b-f, arising through the further reactions of 7b-h, were isolated from these reactions. Reasonable mechanisms have been suggested for the formation of the different products in the irradiation of 5b-h.

Laser flash photolysis studies involving direct excitation and triplet sensitization of 5b-h have also been carried out. From the observed triplet lifetimes, the aryl group migration rates have been estimated at $\leq 1 \times 10^6 \, s^{-1}$.

Note : The numbers of the various compounds given here correspond to those given under the respective chapters.

CHAPTER I

PHOTOCHEMICAL TRANSFORMATIONS OF A FEW BRIDGEHEAD-SUBSTITUTED DIBENZOBARRELENES

I.1 ABSTRACT

The photochemical transformations of a few bridgehead-substituted dibenzobarrelenes such as 11,12-dibenzoyl-9,10-dihydro-9-hydroxymethyl-9,10-ethenoanthracene (4f), 11,12-dibenzoyl-9,10-dihydro-9-ethyl-9,10-ethenoanthracene (4g), 9-benzyl-11,12-dibenzoyl-9,10-dihydro-9,10-etheno-anthracene (4h), 9-cyclopentyl-11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracene (4i), 11,12-dibenzoyl-9,10-dihydro-9-isopropyl-9,10-ethenoanthracene (4j), 9-cyclohexyl-11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracene (4k), and 9-cycloheptyl-11,12-dibenzoyl-9,10-dihydro-9,10-etheno-anthracene (4l) have been investigated by steady-state irradiation and laser flash photolysis. Flash photolysis studies of a few closely related barrelene systems such as 11,12-dibenzoyl-9,10-dihydro-9-hydroxy-9,10-ethenoanthra-cene (4a), 11,12-dibenzoyl-9,10-dihydro-9-methoxy-9,10-etheno-anthracene (4b), 9-acetoxy-11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracene (4c), 9-cyano-11,12-dibenzoyl-9,10-di-

hydro-9,10-ethenoanthracene (4d), and 11,12-dibenzoyl-
9,10-dihydro-9-formyl-9,10-ethenoanthracene (4e) have also
been examined through laser flash photolysis studies. The
dibenzobarrelenes 4a-1 have been prepared by the reaction
of dibenzoylacetylene (DBA) with the corresponding anthra-
cenes.

Irradiation of the dibenzobarrelenes 4f-h in benzene,
methanol and acetone gave 4b- or 8b-substituted dibenzo-
semibullvalenes 5f,g, 6g,h or products derived from them.
However, the irradiation of 4i yielded a mixture of the
corresponding 4b-substituted dibenzosemibullvalene 5i and
the dibenzocyclooctatetraene 16i. In contrast, the irra-
diation of 4j-1 in various solvents gave the corresponding
dibenzocyclooctatetraenes 16j-1, exclusively. The irra-
diation of dibenzobarrelenes 4a-e has been reported earlier
to give the corresponding 4b- or 8b-substituted dibenzo-
semibullvalenes.

Laser flash photolysis studies of 4f-k have been
carried out to examine the nature of the transients involved
in their photorearrangements. As model systems, the closely
related dibenzobarrelenes 4a-e have also been examined by
laser flash photolysis. The 337.1 nm laser flash photolysis
of 4a-k in benzene results in the formation of their triplets
in high yields (Φ_T = 0.6-1.0). The triplets, in general, are

short lived (0.03-11 μs) and are readily quenched by
oxygen, di-tert-butyl nitroxide and ferrocene
(k_q^T = (0.2-8) x 10^9 $M^{-1}s^{-1}$). In spite of the high Φ_T's,
the reluctance of a few dibenzobarrelenes such as 4j-1 to
undergo the barrelene-semibullvalene rearrangement, under
steady-state irradiation, appears to be related to the
unusually short lifetimes of their triplets. Decay modes,
other than those leading to dibenzosemibullvalenes may be
available for these triplets.

I.2 INTRODUCTION

Zimmerman and Grunewald[1] had observed that barrelene (1)
undergoes a facile photoisomerization of the di-π-methane
type[2-4] to give semibullvalene (2). Further investigations
revealed that 2 is formed under sensitized irradiation of 1,
whereas direct irradiation leads to the formation of cyclo-
octatetraene (3)[5-7] (Scheme I.1). Numerous reports have
appeared in the literature on the phototransformations of
barrelenes,[8,9] benzobarrelenes,[10-16] naphthobarrelenes,[17-21]
dibenzobarrelenes,[22-32] other barrelene derivatives[33,34]
and related systems.[35-47] Diradical intermediates have been
postulated in the rearrangement of some barrelene deriva-
tives, leading to the corresponding semibullvalenes.[48] Also,
it has been suggested that both vinyl and bridgehead sub-
stituents present in the barrelene substrates have pronounced

4

Scheme 1.1

$\left[T^1 \right]^*$ ⟶ **2**

$\left[S^1 \right]^*$ ⟶ **3**

1
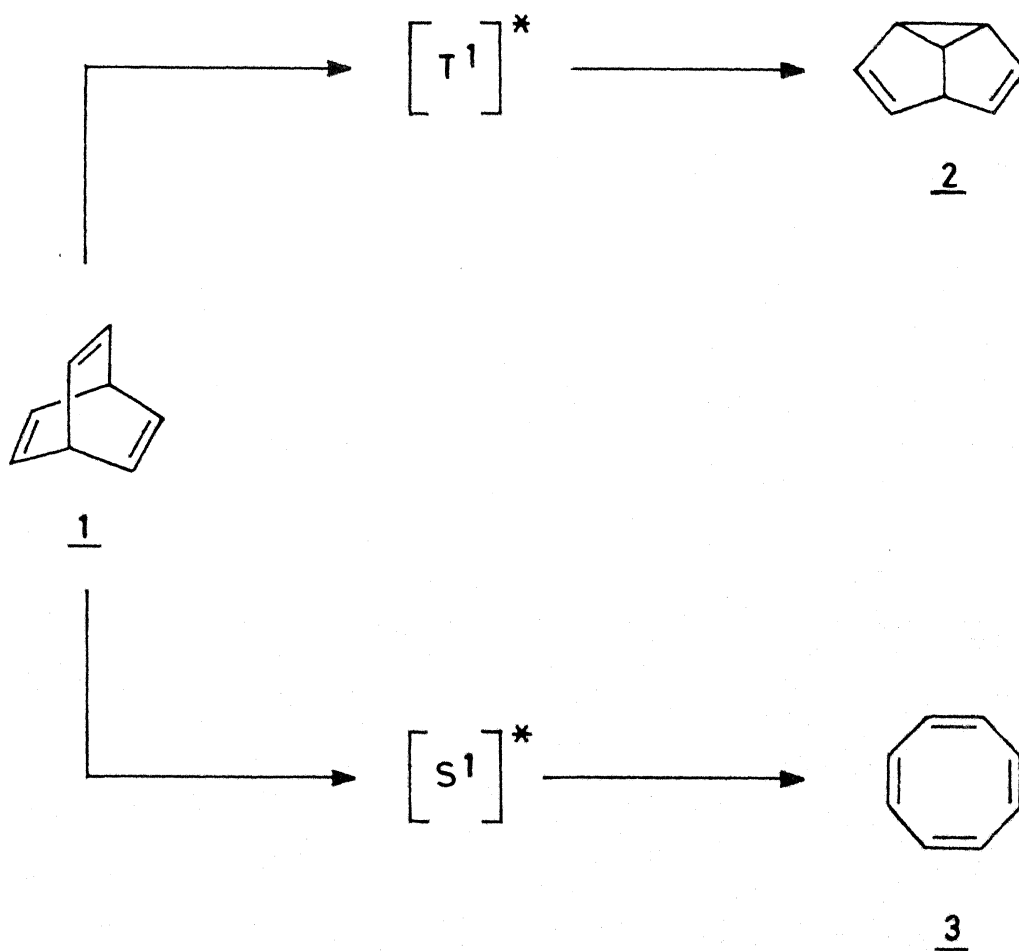
effect on the observed regioselectivity in these rearrange-
ments. The observed regioselectivity has been explained
in terms of the preferential stabilization of the diradical
intermediates by through-bond or through-space interaction
with the substituents.[22-28]

The photochemical rearrangements of several bridgehead-
substituted dibenzobarrelenes containing 1,2-dibenzoylalkene
moiety have been reported recently from this laboratory.[29-32]
These substrates, in principle, are capable of undergoing
reactions characteristic of both 1,2-dibenzoylalkene[49] and
barrelene chromophores. However, these substrates have been
found to undergo photochemical transformations characteristic
of the barrelene chromophore.[29-32] Further, it has been
observed that the bridgehead substituents affect the regio-
selectivity in the rearrangement of barrelenes to semibull-
valenes. Thus, the irradiation of dibenzobarrelenes 4a-e
led to the exclusive formation of only one of the two regio-
isomeric dibenzosemibullvalenes 5 or 6[31,32] (Scheme I.2).
The observed regioselectivity has been explained in terms of
the stabilization/destabilization effects of the bridgehead
substituents on the diradical precursors of 5 and 6. Though
the observed regioselectivity could, by and large, be corre-
lated with the electronegativity of the bridgehead substi-
tuents, the involvement of other factors cannot be ruled out.

Scheme I.2

4 a-e

$[T^1]^*$

5 b,c,e

6 a,d

a)	R = OH
b)	R = OCH₃
c)	R = OCOCH₃
d)	R = CN
e)	R = CHO

Scheme I.2

$\underline{4}$ a-e

$[T^1]^*$

$\underline{5}$ b,c,e

$\underline{6}$ a,d
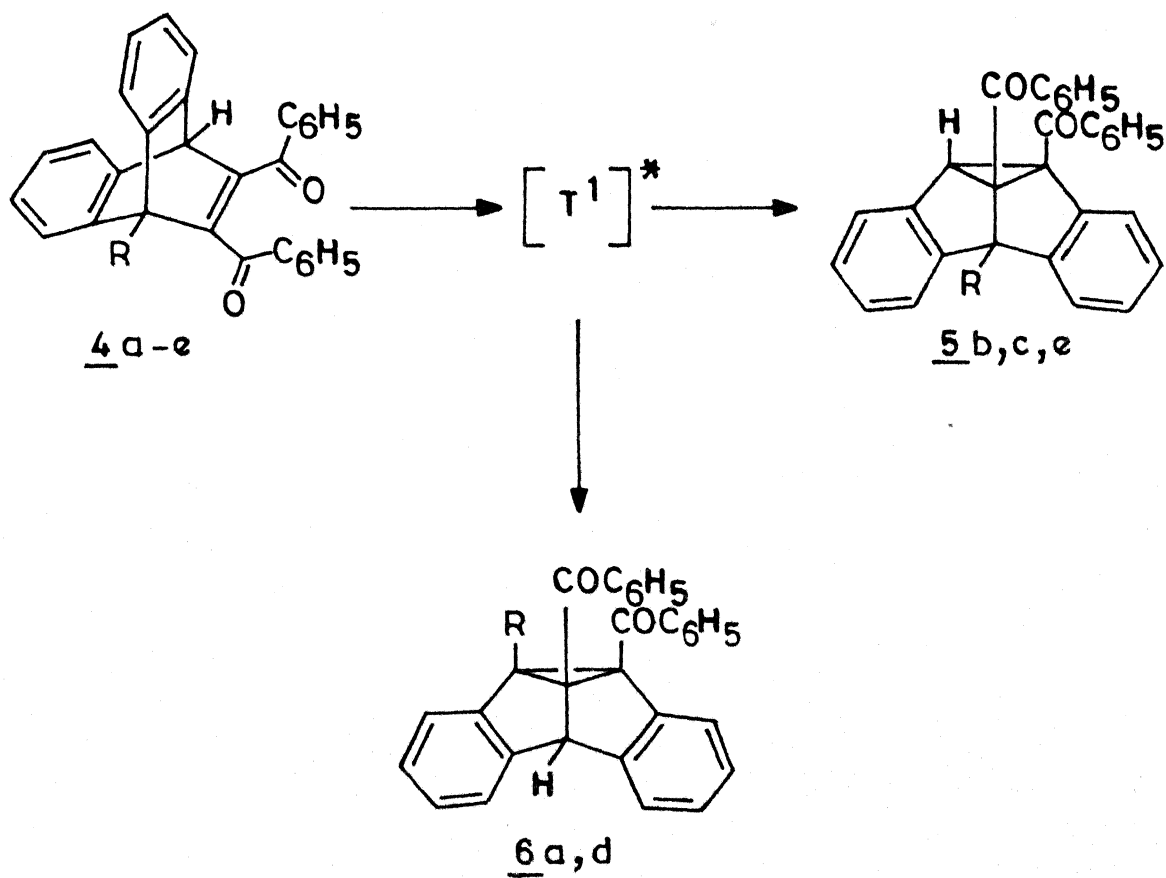
a)	R = OH
b)	R = OCH_3
c)	R = $OCOCH_3$
d)	R = CN
e)	R = CHO

The effect of steric factors, for example, has hitherto not been systematically explored.

In the present studies, we have examined in detail, the photochemistry of several dibenzobarrelenes containing 1,2-dibenzoylalkene components, having substituents of comparable electronegativities, but of varying sizes at the bridgehead position to examine the effect of steric factors on the regioselectivity of barrelene-semibullvalene rearrangement and also to characterize the transients involved in these rearrangements by laser flash spectroscopy. The dibenzobarrelenes that we have examined include 11,12-dibenzoyl-9,10-dihydro-9-hydroxymethyl-9,10-ethenoanthracene (<u>4f</u>), 11,12-dibenzoyl-9,10-dihydro-9-ethyl-9,10-etheno-anthracene (<u>4g</u>), 9-benzyl-11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracene (<u>4h</u>), 9-cyclopentyl-11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracene (<u>4i</u>), 11,12-dibenzoyl-9,10-dihydro-9-isopropyl-9,10-ethenoanthracene (<u>4j</u>), 9-cyclohexyl-11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracene (<u>4k</u>), and 9-cycloheptyl-11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracene (<u>4l</u>). In addition, the laser flash photolysis studies of a few closely related barrelenes with known photochemistry[31,32] have also been examined. These include 11,12-dibenzoyl-9,10-dihydro-9-hydroxy-9,10-etheno-anthracene (<u>4a</u>), 11,12-dibenzoyl-9,10-dihydro-9-methoxy-

9,10-ethenoanthracene (4b), 9-acetoxy-11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracene (4c), 9-cyano-11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracene (4d), and 11,12-dibenzoyl-9,10-dihydro-9-formyl-9,10-ethenoanthracene (4e).

I.3 RESULTS AND DISCUSSION

I.3.1 Preparation of Starting Materials. A convenient method of preparing dibenzobarrelenes containing 1,2-dibenzoylalkene moieties is through the reaction of anthracenes with dibenzoylacetylene (DBA), either by direct heating[50] or in the presence of a suitable catalyst such as anhydrous aluminium chloride.[51] We have prepared the dibenzobarrelenes 4h-l in high yields by the anhydrous aluminium chloride catalysed addition of DBA to the corresponding anthracene derivatives. The dibenzobarrelene 4f, however, was prepared by refluxing an equimolar mixture of 9-hydroxymethylanthracene and DBA in dry toluene. The structures of 4f-l have been established on the basis of analytical results, spectral evidence and comparison of spectral data with those reported in literature, wherever applicable. The dibenzobarrelenes 4a-e,g were prepared by reported procedures.[31,32]

I.3.2 <u>Preparative Photochemistry and Product Identi-
fication</u>. The irradiation of a benzene solution of <u>4f</u> for
1/4 h gave a 64% yield of 8c,8d-dibenzoyl-4b-hydroxymethyl-
4b,8b,8c,8d-tetrahydrodibenzo[a,b]cyclopropa[c,d]pentalene
(<u>5f</u>). Similarly, the irradiation of <u>4f</u> in methanol and
acetone, under analogous conditions, gave <u>5f</u> in 82% and 79%
yields, respectively. The structure of <u>5f</u> has been arrived
at on the basis of analytical results and spectral evidence.
The IR spectrum of <u>5f</u>, for example, showed absorptions at
3470 and 3320 cm^{-1}, due to free and hydrogen bonded OH,
respectively. The carbonyl absorption was observed at
1650 cm^{-1}. The ^1H NMR spectrum of <u>5f</u> (Figure I.1) showed a
broad singlet at δ 2.40 (1 H, D_2O exchangeable), assigned
to the OH proton. The broad singlet at δ 4.60 (2 H) is
assigned to the methylene protons, whereas the singlet at
δ 4.70 (1 H) is assigned to the H-8b proton. The aromatic
protons (18 H) appeared as a complex multiplet centred
around δ 7.35. The mass spectrum of <u>5f</u> showed the molecular
ion peak at m/e 442 and the fragmentation patterns are in
agreement with the assigned structure.

The irradiation of <u>4g</u> in benzene, however, gave a mix-
ture of 8c,8d-dibenzoyl-4b-ethyl-4b,8b,8c,8d-tetrahydrodi-
benzo[a,b]-cyclopropa[c,d]pentalene (<u>5g</u>, 62%), an isomeric

Scheme I.3

f) R = CH$_2$OH
g) R = CH$_2$CH$_3$
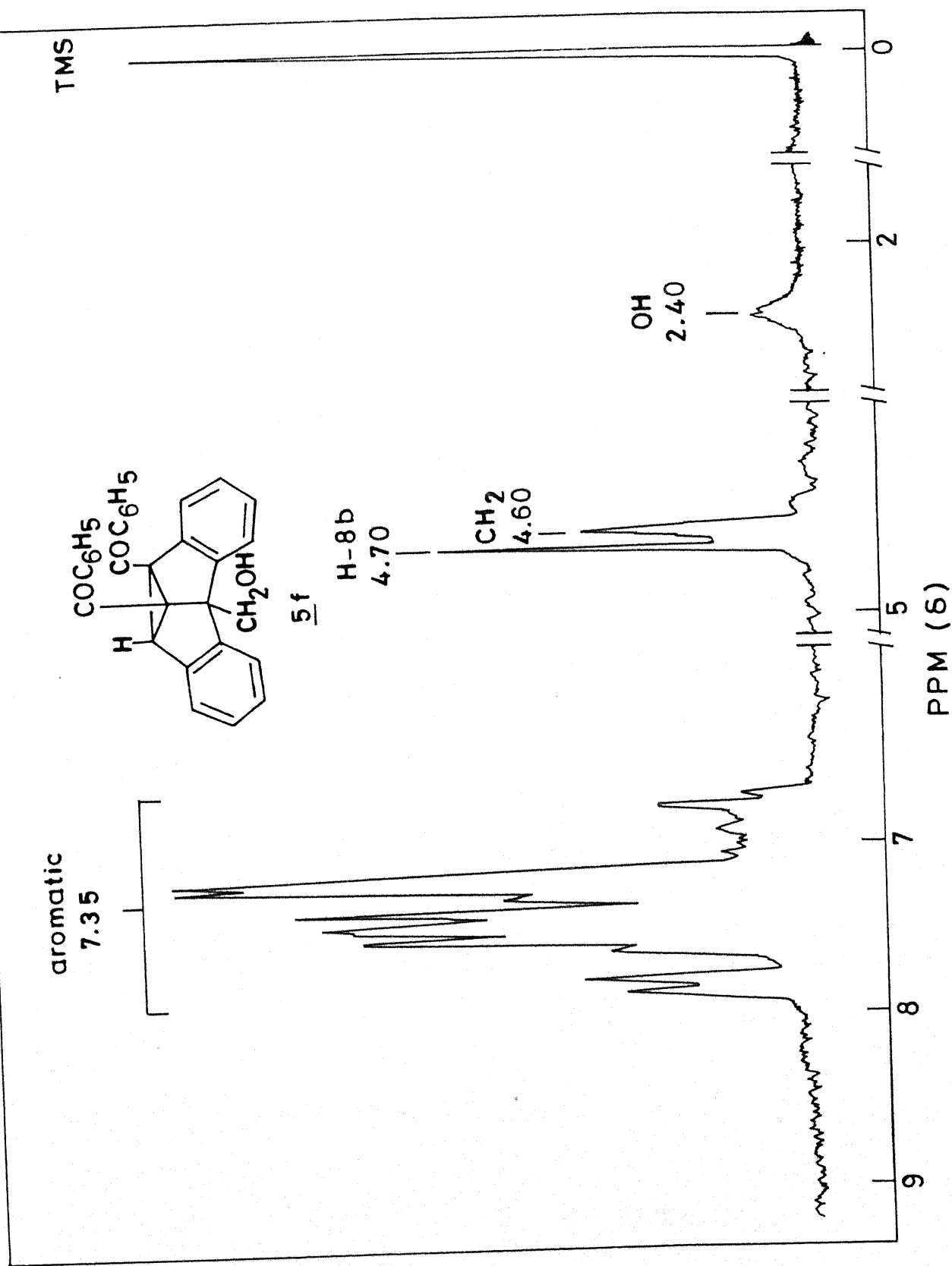h) R = CH$_2$C$_6$H$_5$
i) R = C$_5$H$_9$
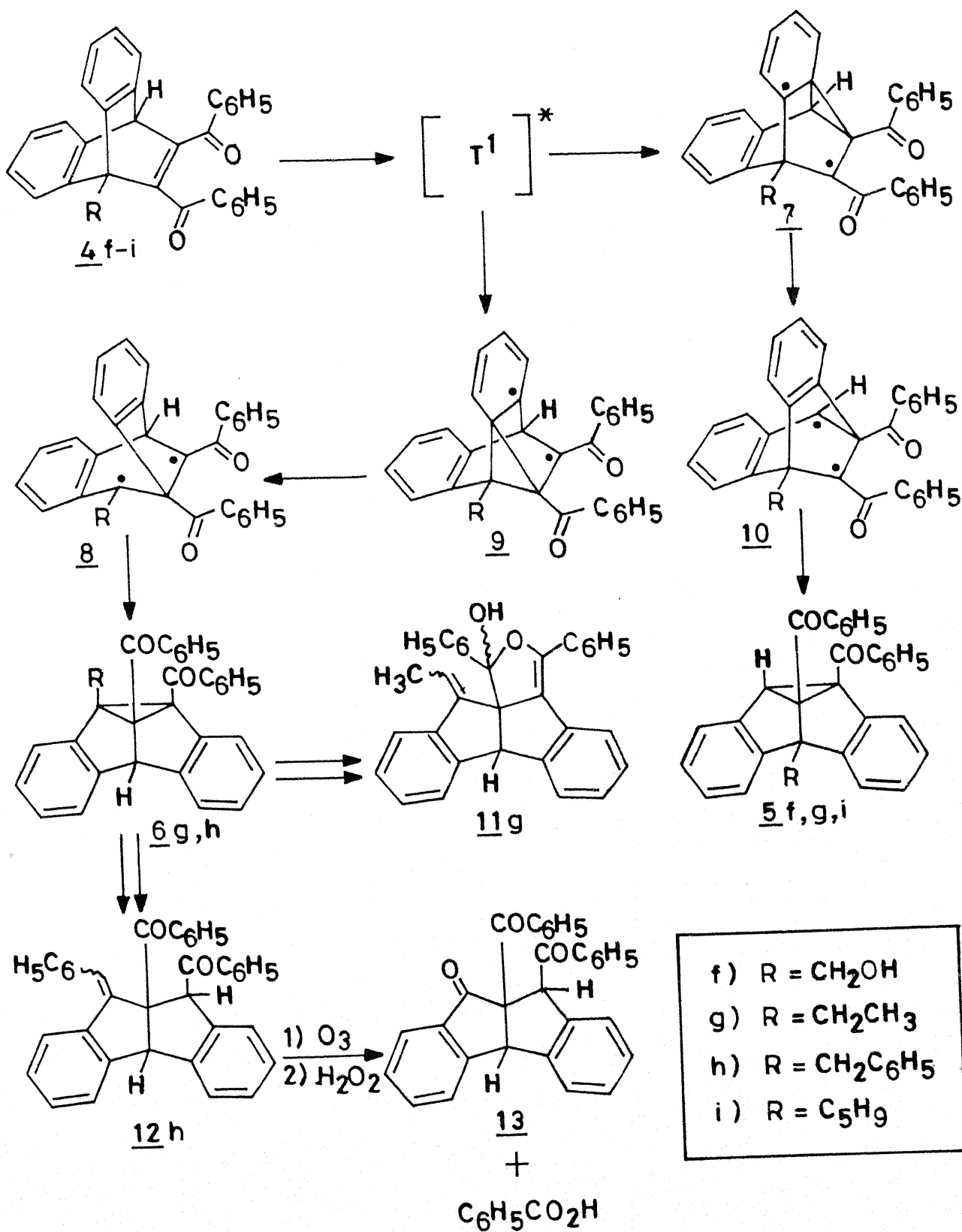
Figure I.1 ^{1}H NMR spectrum (90 MHz) of 5 f.

hydroxy compound 11g (18%), derived from 8c,8d-dibenzoyl-
8b-ethyl-4b,8b,8c,8d-tetrahydrodibenzo[a,b]cyclopropa[c,d]-
pentalene (6g), and unchanged 4g (3%). Similarly, the irra-
diation of 4g in methanol gave a mixture of 5g (68%), 11g
(13%), and unchanged 4g (3%). However, the irradiation of
4g in acetone gave a mixture of 5g (63%), 11g (19%), an
isomeric lactone 20 (2%), and unchanged 4g (3%). The
structures of 11g and 20 have been arrived at on the basis
of analytical results and spectral data. The IR spectrum
of 11g, for example, showed an OH absorption band at
3500 cm^{-1} and did not show any carbonyl absorptions. The
^{1}H NMR spectrum of 11g (Figure I.2) showed a doublet at
δ 1.30 (3 H, J = 7.5 Hz), assigned to the methyl protons.
The broad signal at δ 3.20 (1 H, D_2O exchangeable) has been
assigned to the OH proton, whereas the singlet at δ 4.60
(1 H) has been assigned to H-4b. The vinylic proton
appeared as a quartet at δ 5.20 (1 H, J = 7.5 Hz) and the
aromatic protons appeared as a multiplet centred around
δ 7.60 (18 H). The IR spectrum of 20 showed a carbonyl
absorption at 1750 cm^{-1}, characteristic of γ-lactones.
The ^{1}H NMR spectrum of 20 (Figure I.3) showed a triplet at
δ 1.50 (3 H, J = 7.5 Hz) due to the methyl protons and a
quartet at δ 2.80 (2 H, J = 7.5 Hz) due to the methylene
protons. The bridgehead proton appeared as a sharp
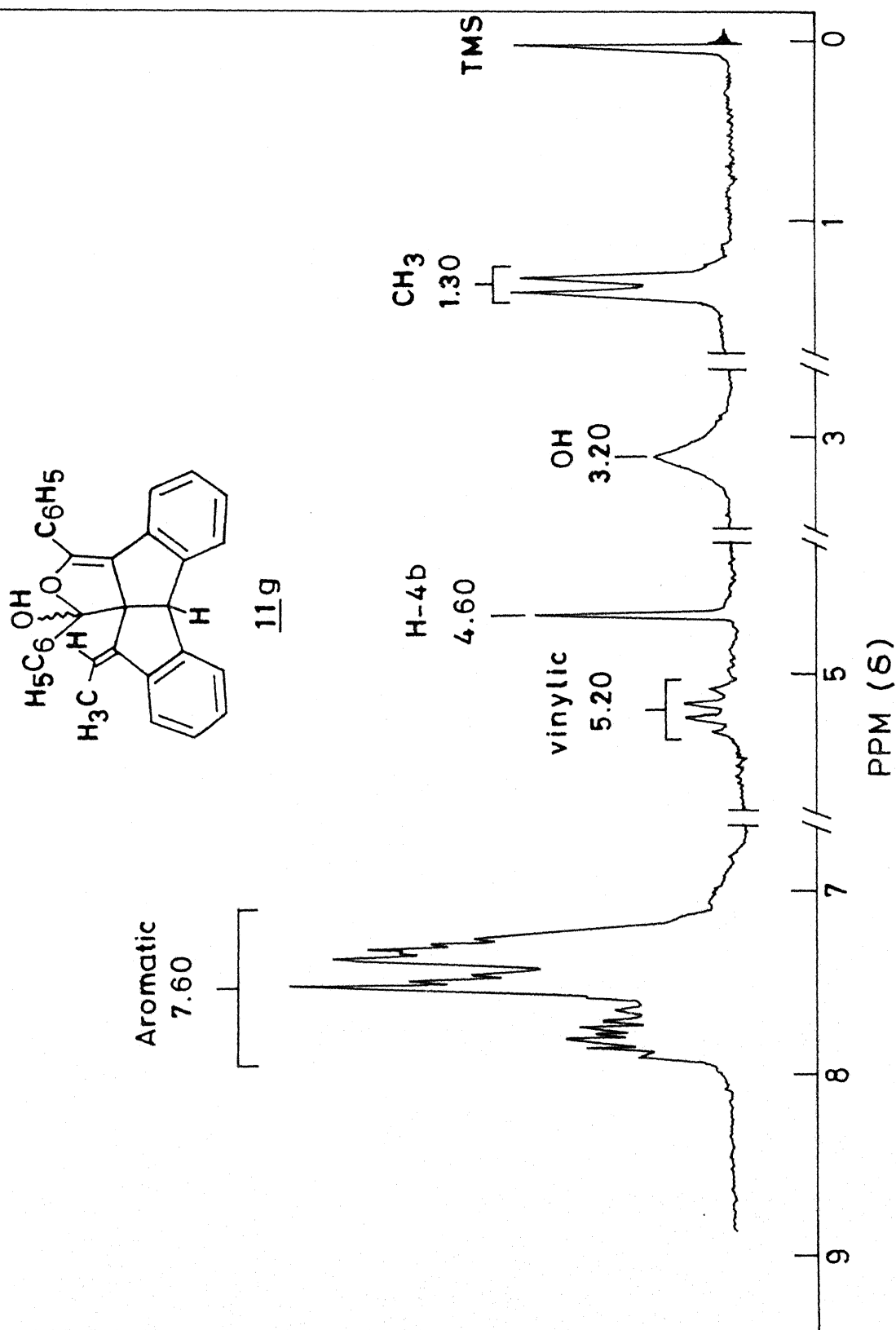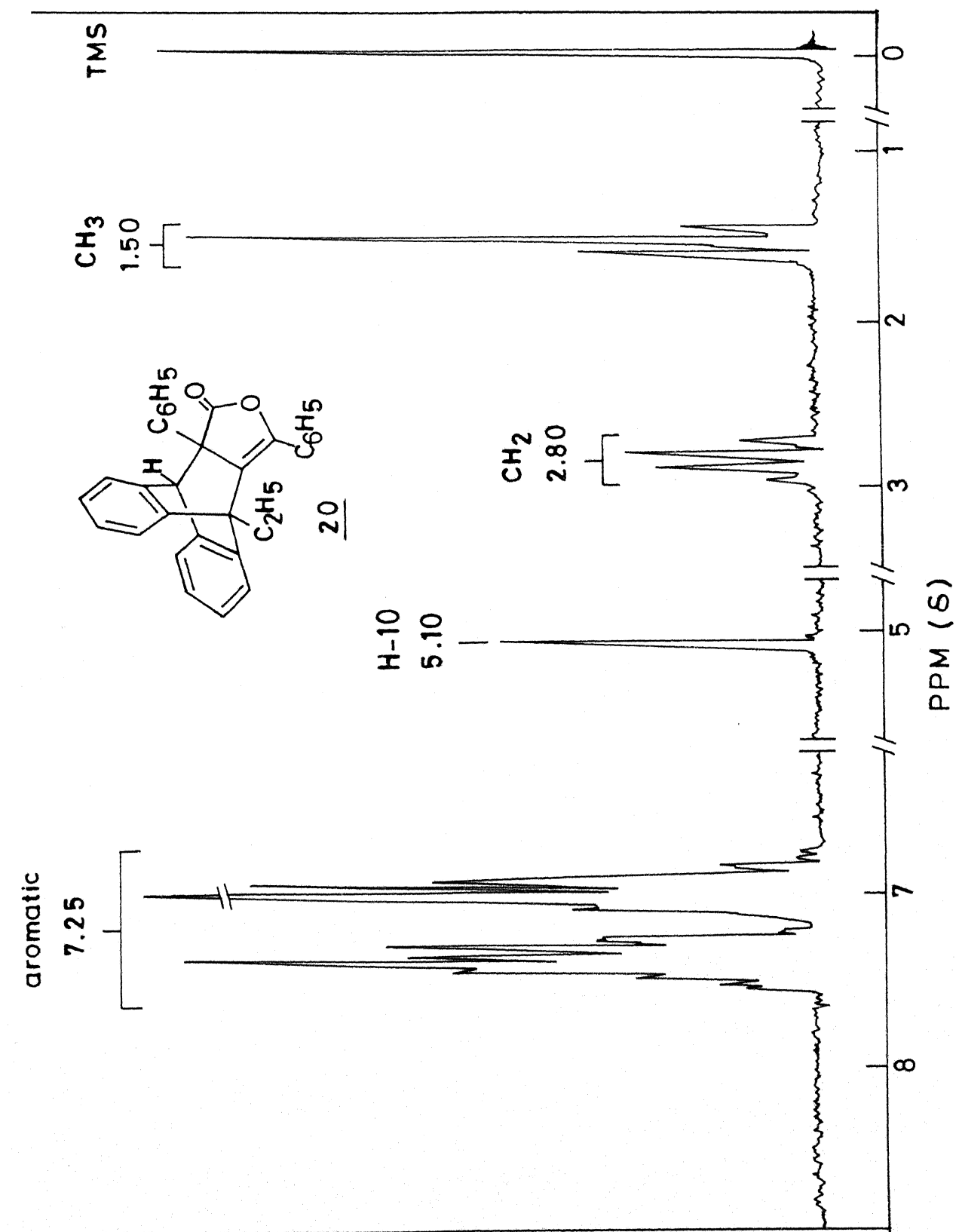
Figure I.2 ^{1}H NMR spectrum (90 MHz) of 11g.

Figure I.3 ^{1}H NMR spectrum (90 MHz) of 20 .

singlet at δ5.1 (1 H). The aromatic protons appeared as
a complex multiplet centred around δ7.25 (18 H).

The irradiation of 4h in different solvents, on the
other hand, gave 9-benzylidene-9a,10-dibenzoyl-4b,9,9a,10-te-
trahydro-cis-indeno[1,2-a]indene (12h, 18-22%), derived from
the 8b-substituted semibullvalene 6h, along with appreciable
amounts (42-56%) of the unchanged starting material 4h. The
structure of 12h has been arrived at on the basis of analy-
tical results, spectral data and chemical transformations.
Ozonolysis of 12h, for example, gave a mixture of 9a,10-di-
benzoyl-9-oxo-4b,9,9a,10-tetrahydro-cis-indeno[1,2-a]indene
(13, 57%) and benzoic acid (14, 50%) (Scheme I.3).

Irradiation of 4i in benzene gave a mixture of 4b-cyclo-
pentyl-8c,8d-dibenzoyl-4b,8b,8c,8d-tetrahydrodibenzo[a,b]-
cyclopropa[c,d]pentalene (6i, 18%), 5-cyclopentyl-1,4-diben-
zoyl-2,6-dibenzocyclooctatetraene (16i, 25%), and unchanged
4i (20%). Likewise, the irradiation of 4i in methanol and
acetone gave a mixture of 6i (21-23%), 16i (21-23%), and
unchanged 4i (20%), in each case. In contrast to the
irradiation of 4f-i, the irradiation of 4j in different sol-
vents gave the corresponding cyclooctatetraene 16j (21-22%),
as the only isolable product, along with appreciable amounts
(45-51%) of the unchanged starting material 4j. Similarly,

Scheme I.4

i) R = C_5H_9

j) R = $CH(CH_3)_2$

k) R = C_6H_{11}

l) R = C_7H_{13}
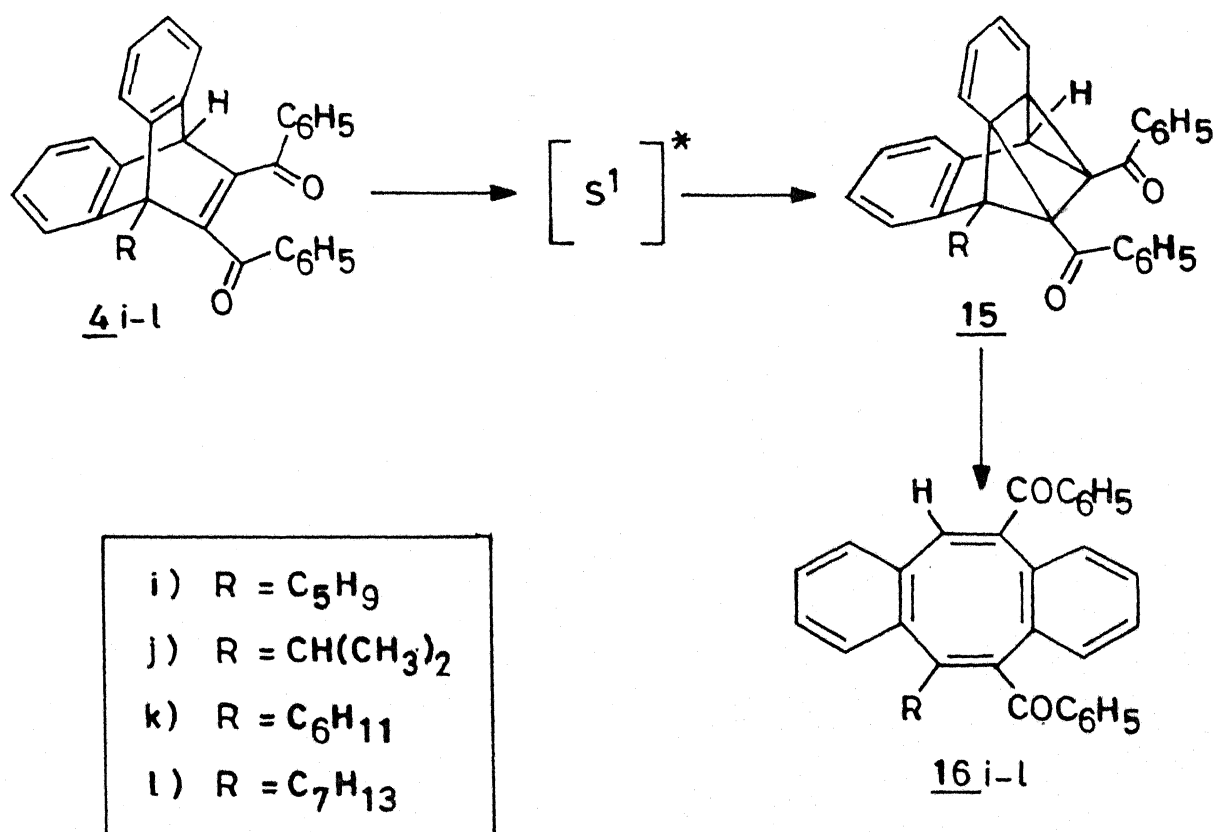
the photolysis of 4k and 4l in different solvents gave the corresponding cyclooctatetraenes 16k (46-55%) and 16l (70-88%), respectively.

Since dibenzobarrelenes 4i-l gave the singlet mediated products (the dibenzocyclooctatetraenes 16i-l) under direct irradiation conditions, attempts were made to carry out the irradiations of 4i-l, under sensitized conditions, using biacetyl ($\lambda_{max} \simeq 450$ nm) as triplet sensitizer under conditions wherein the sensitizer alone absorbed the light. Thus, the irradiation of 4i-l in benzene in the presence of excess of biacetyl using the output from a Hanovia 450 W medium pressure mercury lamp (selectively filtered through a pyrex glass sleeve and a 0.02% (w/v) solution of 9,10-dibromoanthracene in toluene[52]), did not lead to any product formation; most of the starting materials 4i-l could be recovered unchanged, in each case.

I.3.3 <u>Laser Flash Photolysis Studies</u>.[53] In order to shed light on the precursors and intermediates that lead to the photoproducts, observed under steady-state photolysis, the dibenzobarrelenes 4a-k were examined by laser flash photolysis. Nitrogen laser pulses (337.1 nm, 8 ns, 2-3 mJ) were employed for laser excitation. The transients were observed over 0.1-100 μs following the laser excitation and

were characterized by broad and diffuse absorption spectra
extending beyond 700 nm. These were assigned primarily to
the triplets of the dibenzobarrelenes on the basis of
quenching effects of oxygen, di-tert-butyl nitroxide (DTBN,
stable free radical) and ferrocene. For substrates 4a-e,g,
in addition, azulene, β-carotene and p-methoxyphenol were
employed as triplet quenchers. With β-carotene as quencher,
growth of intense transient absorption due to β-carotene
triplet was observed at 510-550 nm at the same time scale
as that of the decay of the dibenzobarrelene triplets,
monitored at 600-700 nm. That hydrogen abstraction occured
in the course of the quenching of dibenzobarrelene triplets
by p-methoxyphenol was shown by the formation of p-methoxy-
phenoxy radical with a characteristic absorption spectrum
at 370-430 nm (λ_{max} = 405 nm).[54-56] The quenching of diben-
zobarrelene triplets follows pseudo-first order kinetics.
The plots with p-methoxyphenol as quencher are shown in
Figure I.4.

To confirm the triplet assignment for the transients,
triplet sensitization experiments using 4f-k as acceptors
were carried out. Attempts to generate the triplet of 4f
via energy transfer from di-tert-butylthioketone
(E_T = 45 kcal mol^{-1})[57] under 532 nm laser excitation and
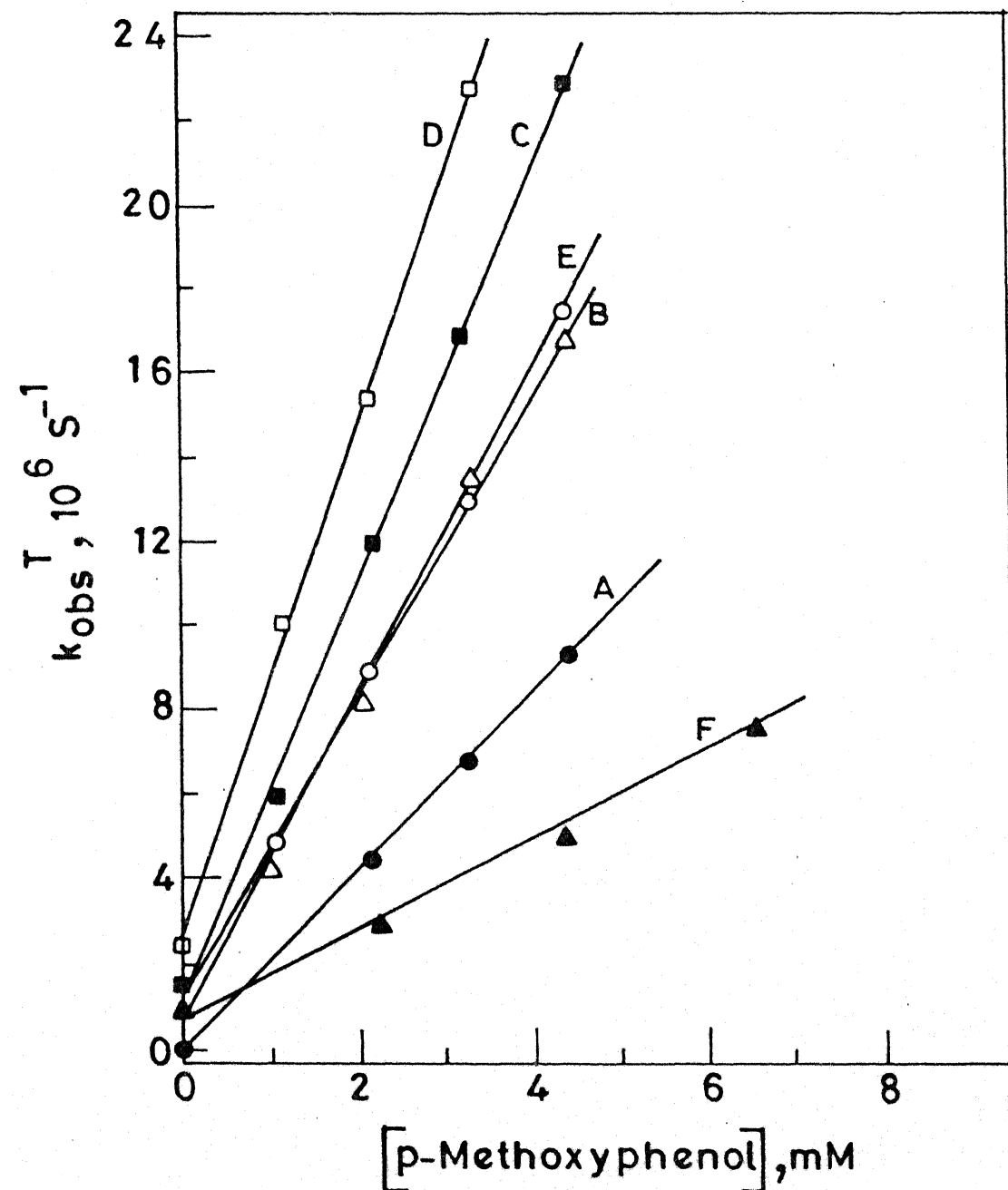
Figure I.4 Plots of pseudo-first order rate constants for triplet decay vs. p-methoxyphenol concentrations in benzene. The substrates are 4a (A), 4b (B), 4c (C), 4d (D), 4e (E), and 4g (F).

from camphorquinone (E_T = 52 kcal mol^{-1})[58] under 485 nm laser excitation in the presence of millimolar concentration of 4f in benzene were not successful. This apparently may be due to the fact that the spectroscopic triplet energy of dibenzobarrelenes is higher or close to the E_T's of these two sensitizers. In addition, the inefficiency of exchange interaction in energy transfer involving the sterically crowded donor and acceptor has also to be reckoned with.

Pulse radiolysis technique[53,59] has also been employed to generate the triplets of a few representative dibenzo-barrelenes such as 4a,d-g. In this method, deaerated benzene solutions containing biphenyl at a high concentration (0.1 M) and a substrate at a relatively low concentration ($\leq$5 mM) was irradiated with 5 ns electron pulses. Biphenyl triplet (λ_{max}^T = 360 nm) produced as a result of energy transfer from the shortlived benzene triplet (pulse-radiolytic) subsequently acted as an excitation donor to the substrates. The formation of the triplets of dibenzobarre-lenes was observed at long wavelengths (450-600 nm). The transient absorption spectra and decay behaviours following the enhanced decay of 4a,d-g agreed well with those observed under direct laser excitation (337.1 nm) of these sub-strates. These results, along with quenching behaviours

described earlier, strongly favour the assignment of the laser-flash-photolytic transients as triplets. In the case of 4f, the comparison of absorbance due to biphenyl triplet (donor) and the triplet of 4f (acceptor) made it possible to estimate[59] the maximum extinction coefficient (ε_{max}^{T}) of the latter at 4×10^3 $M^{-1}cm^{-1}$ (at 490 nm). This method could not be reliably used for 4h-k because of their short triplet lifetimes (< 1 μs). The ε_{max}^{T} values for 4a-e,g were estimated by known methods.[30,60]

The triplet yields (Φ_T) of 4a-k were determined in optically matched benzene solutions at the laser excitation wavelength (337.1 nm). The formation of benzophenone triplet ($\Phi_T = 1$, $\varepsilon_{max}^{T} = 7.6 \times 10^3$ $M^{-1}cm^{-1}$ at 532 nm[61] in benzene) was used for actinometry. To obtain Φ_T, the end-of-pulse absorbance change due to the substrate triplet divided by its extinction coefficient was compared with that for benzophenone. For substrates 4h-k, since ε_{max}^{T} values could not be reliably estimated, ε_{max}^{T} was assumed to be equal to that of 4g, namely 5×10^3 $M^{-1}cm^{-1}$. The spectral and kinetic data of the triplets of 4a-k are given in Table I.1. The linear plots of pseudo-first order rate constants for the decay of dibenzobarrelene triplets against quencher concentrations gave the bimolecular rate constants

Table I.1   Absorption Spectral and Kinetic Data of the
Triplets of Dibenzobarrelenes 4a-k in Benzene

substrate	λ_{max}, T^{a} nm	ε_{max}, T^{b} 10^3 $M^{-1}cm^{-1}$	$\tau_{T}, {}^{c}$ μs	$\Phi_{T} {}^{b}$
4a	430	3	11.0	0.7
4b	~390	6	1.2	0.6
4c	510	7	0.85	0.7
4d	510	6	0.34	0.7
4e	~410	6	1.8	0.6
4f	490	4	2.2	1.0
4g	510	5	1.0	0.7
4h	500	–	0.65	0.7
4i	520	–	0.46	0.9
4j	540	–	0.10	0.7
4k	540	–	0.03	0.7

$\underline{a}$ $\pm$ 10 nm . $\underline{b}$ $\pm$ 30% . $\underline{c}$ $\pm$ 15% .

(k_q^T) for quenching. The data concerning k_q^T are presented in Table I.2.

In Figures I.5-I.8, several absorption spectra and kinetic traces in benzene for the transients of 4a-k are presented. A close examination of the transient spectra reveals several interesting features. For 4a, in addition to a relatively long-lived triplet (τ_T = 11 µs, λ_{max} = 325, 430, and 670 nm), the transient spectra (Figure I.5 A, A') show a photoproduct (λ_{max} = 325 nm), persisting at the end of the triplet decay. In methanol, the triplet is shorter lived (τ_T = 3 µs) and acts as a precursor for a long-lived transient product ($\tau_T \sim$ 150 µs, λ_{max} = 340 and 450 nm). This species may be the product of hydrogen abstraction by the triplet of 4a. Formation of a species having similar spectral features when the triplet of 4a is quenched by p-methoxyphenol in benzene (in addition to the p-methoxyphenoxy radical) supports this assumption. The triplet of 4b, however, is shorter-lived (τ_T = 1.2 µs in benzene) and gives practically no residual absorption (Figure I.5 B, B') except a small depletion at 310-330 nm. The triplet decay is somewhat slower in methanol (τ_T = 1.6 µs) and there is no indication of hydrogen abstraction by the triplet from methanol. The lower propensity for hydrogen abstraction by

Table I.2 Bimolecular Rate Constants for the Quenching of the Triplets of Dibenzobarrelenes 4a-k in Benzene at 298 K

substrate	$k_q T^a$ 10^9 M^{-1} s^{-1}					
	O_2	DTBN	p-methoxy-phenol	azulene	ferro-cene	β-caro-tene
4a	0.59	0.85	2.2	2.1	6.7	5
4b	0.59	0.49	1.0	0.4	2.1	5
4c	0.28	0.96	5.0	4.6	5.7	7
4d	0.60	1.7	6.1	3.7	6.3	7
4e	0.57	1.2	3.9	1.1	6.4	5
4f	0.54	0.84	–	–	7.9	–
4g	0.48	0.49	3.6	0.75	5.0	4
4h	0.60	0.16	–	–	5.7	–
4i	0.30	0.21	–	–	4.1	–
4j	0.80	0.37	–	–	5.1	–
4k	b	b	–	–	b	–

a ± 10 nm.   b Could not be reliably measured because of the unusually short triplet lifetime.
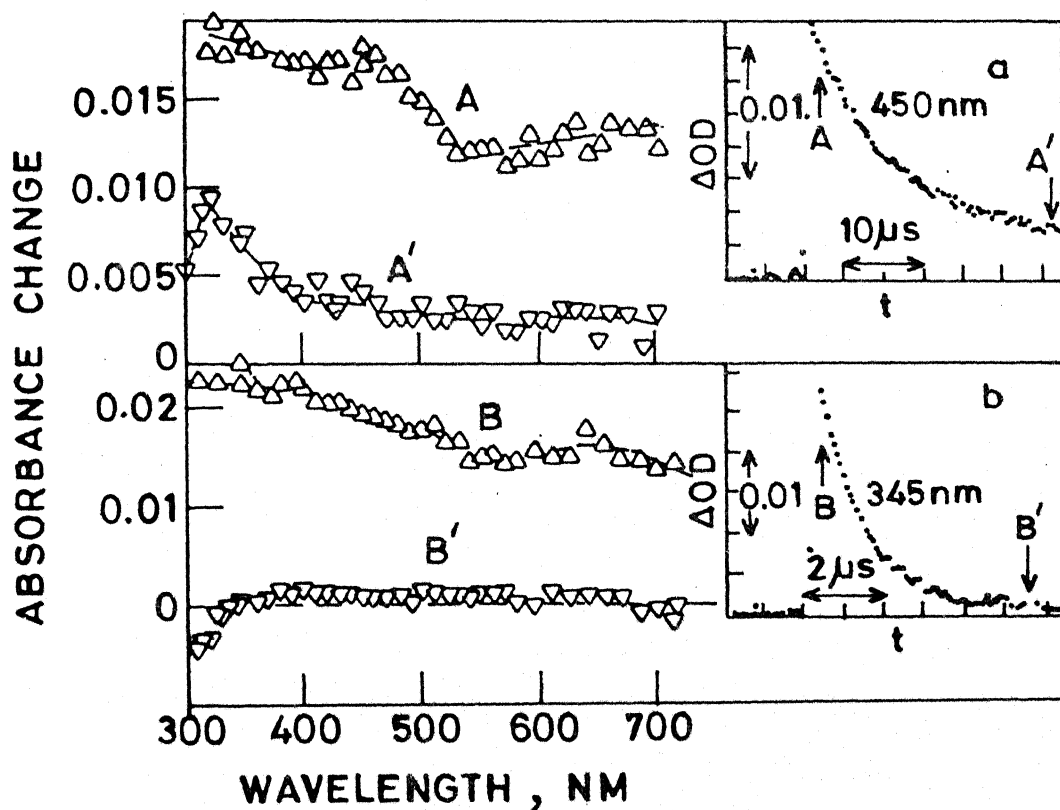
Figure I.5 Transient absorption spectra following 337.1 nm
laser excitation of 4a (A,A') and 4b (B,B'). Insets: kinetic
traces for transient decay of 4a and 4b (b) at the wave-
lengths indicated.

the triplet of 4b is also reflected by the smaller k_q^T for p-methoxyphenol (Table I.2). However, the absorption spectra of the photoproducts by the triplet quenching by p-methoxyphenol bear resemblence to those from 4a, indicating hydrogen abstraction by the triplet of 4b.

The triplets of both 4c and 4d display broad absorption maxima at ~510 nm (Figure I.6 A, A'; B, B') and have their lifetimes lengthened by a factor of ~2, on going from benzene to methanol (Table I.1). The residual absorption, following the decay of triplets of 4c shows a weak band system at 310-340 nm (Figure I.6 A'), while for 4d ground state bleaching is observed (Figure I.6 B').

A prominent feature for 4e in benzene is the formation of a long-lived triplet mediated product with λ_{max} at 320, 410, and 595 nm (Figure I.6 C'). The photoproduct can be a radical from the photocleavage of the formyl group or a diradical generated by the intramolecular formyl hydrogen abstraction by the carbonyl group, followed by the loss of carbon monoxide. The photoproduct in question is not formed in methanol in which the triplet lives nearly as long as in benzene. It is possible that the observed photoproduct in benzene is related to intramolecular hydrogen abstraction,

Figure I.6 Transient absorption spectra following 337.1 nm laser excitation of 4c (A,A'), 4d (B,B'), and 4e (C,C') in benzene. Insets: kinetic traces for transient decay of 4c (a), 4d (b), and 4e (c) at the wavelengths indicated.

the process being less favourable in methanol because of hydrogen bonding of the carbonyl chromophores with the solvent.

The triplets of 4f-h also exhibit broad and diffuse absorption spectra (λ_{max} = 490-510 nm) extending beyond 700 nm in benzene (Figure I.7 A, B, C). The transients decay predominantly by first order kinetics and are efficiently quenched by typical triplet quenchers. Practically no residual absorption (long-lived) is noted in the case of 4f-h. There is no indication of the formation of long-lived photoproducts by intramolecular hydrogen abstraction.

Dibenzobarrelenes 4i-k also exhibit transients having broad and diffuse absorption spectra (λ_{max} = 520-540 nm) extending beyond 700 nm. However, these systems are of considerable interest since long-lived residual absorptions (λ_{max} = 380 and 540 nm) are observed following the decay of the initial transients (Figure I.8 A, A'; B, B'; C, C'). These do not show any sign of decay over the longest possible time scale (~100 μs). The long-lived residual absorptions are due to triplet-mediated photoproducts. This is established by the fact that upon quenching the triplet by ferrocene, the decrease in the residual absorbance occurs
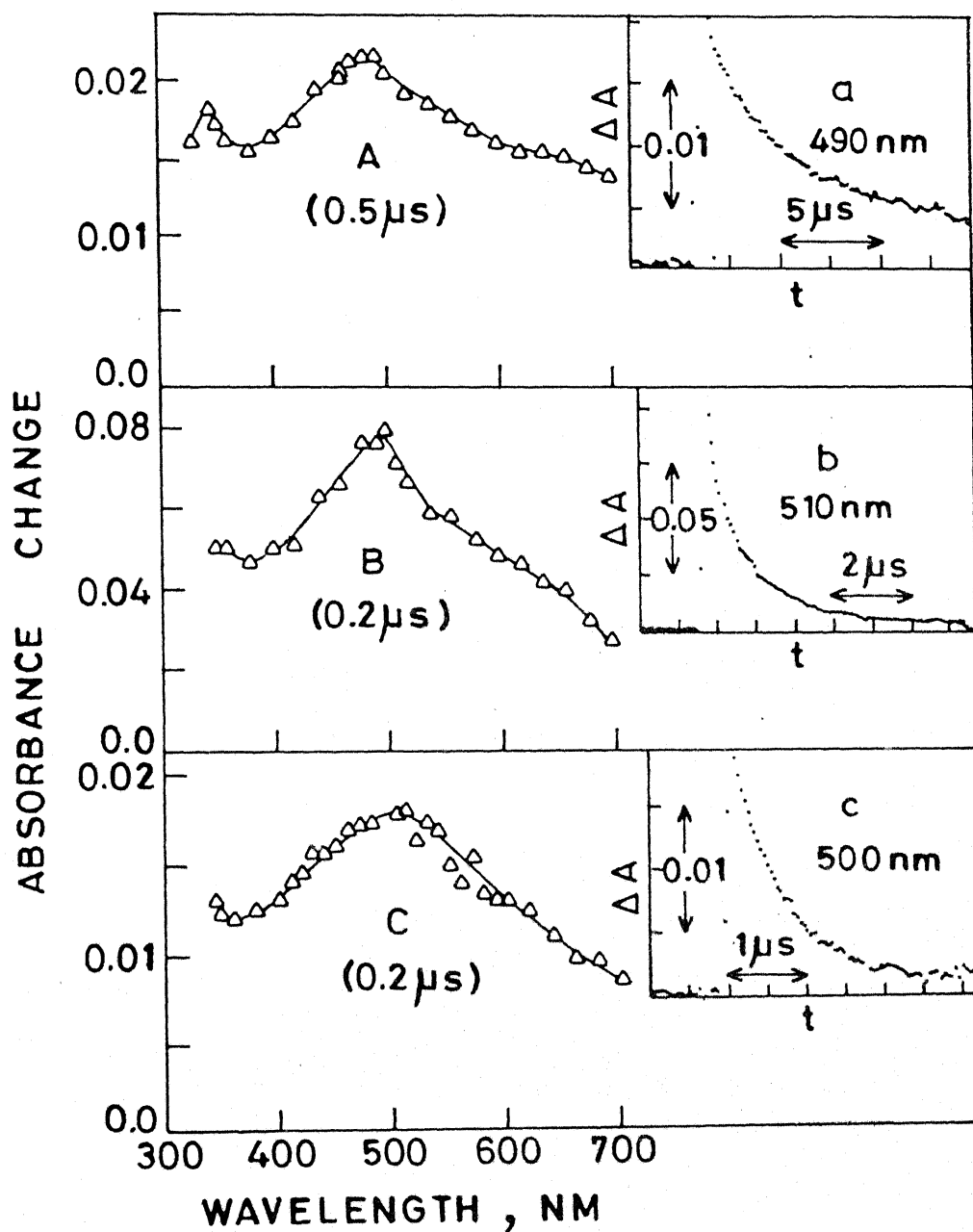
Figure I.7 Transient absorption spectra following 337.1 nm laser excitation of 4f (A), 4g (B), and 4h (C) in benzene. Insets: kinetic traces for transient decay of 4f (a), 4g (b), and 4h (c) at the wavelengths indicated.
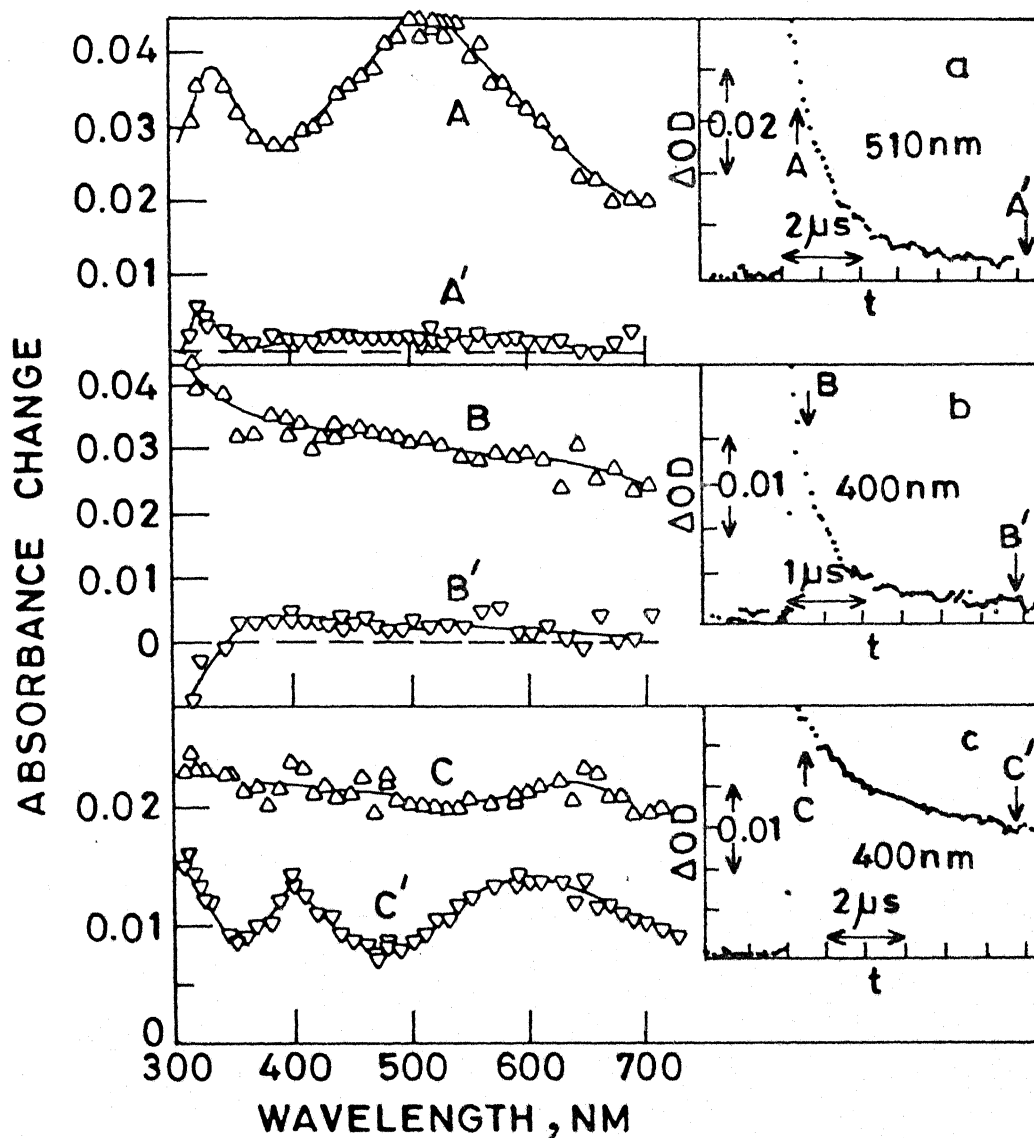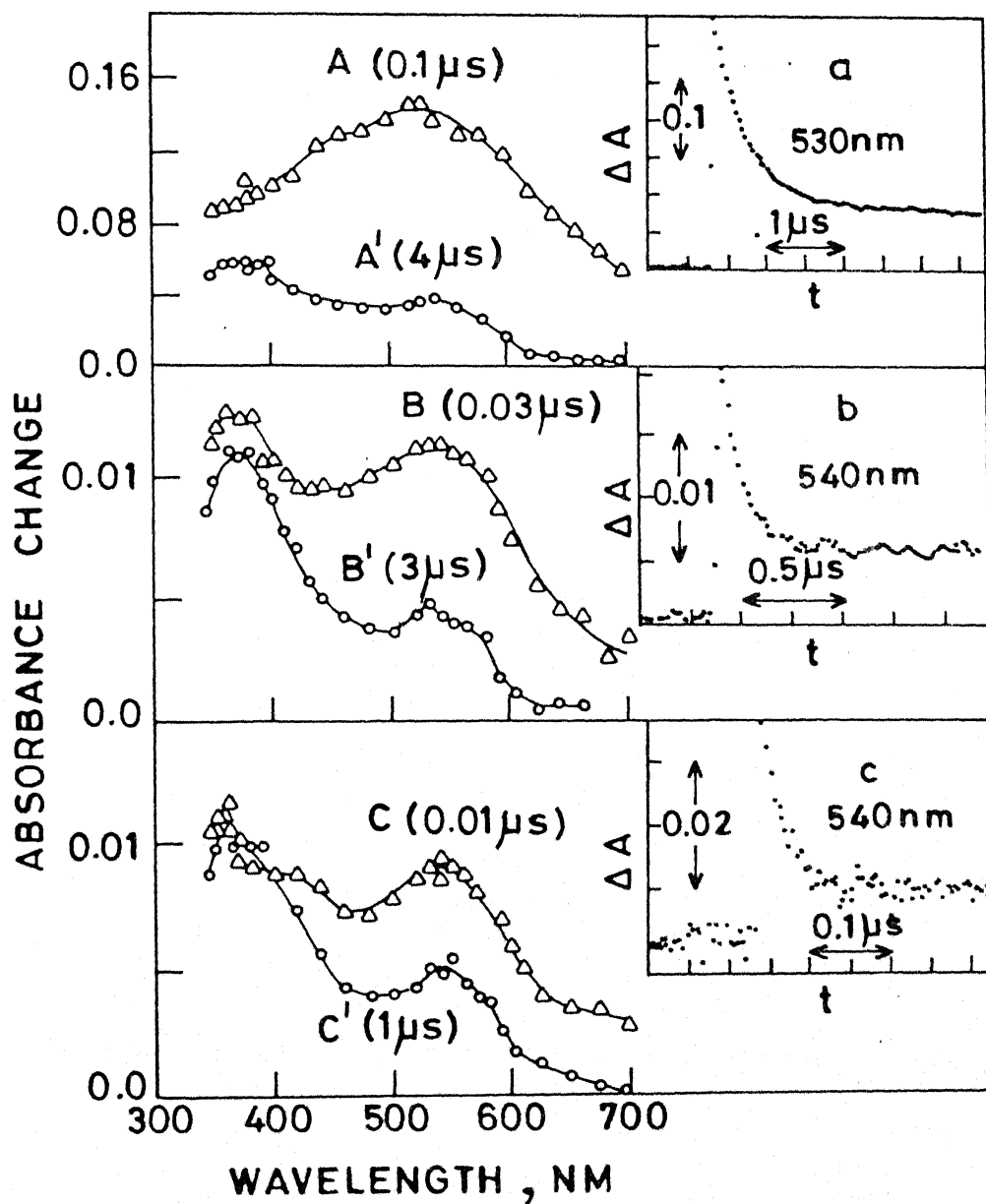
Figure I.8 Transient absorption spectra following 337.1 nm
laser excitation of 4i (A,A'), 4j (B,B'), and 4k (C,C') in
benzene. Insets: kinetic traces for transient decay of
4i (a), 4j (b), and 4k (c) at the wavelengths indicated.

in a manner proportionate to the shortening of the triplet lifetimes. However, no effect of oxygen ($\leq$ 9 mM), DTBN ($\leq$ 30 mM) and ferrocene ($\leq$ 5 mM) was observed on the decay kinetics of the residual absorptions (λ_{max} = 380 and 540 nm) in the case of 4i-k, except for 4j, where the long-lived absorption at and near the short-wavelength maximum (350 nm) was found to undergo partial decay in the presence of oxygen and DTBN.

Although the residual absorptions in the case of 4i-k show no tendancy of decay over the longest available time scale (100 µs), these probably do not represent stable photoproducts because no long-wavelength absorption band systems were found to develop in the solutions of 4i-k that had been extensively photolysed by repetitive laser pulses (337.1 nm). Furthermore, the products (dibenzosemibullvalenes and cyclooctatetraenes) isolated from the photolysates of 4i-k do not absorb at the long-wavelength spectral region (500-600 nm) where the laser-flash-photolytic products exhibit well-defined band systems (parts A'-C', Figure I.8).

I.3.4 Discussion. The formation of dibenzosemibull-valenes and products derived thereof, in the phototransfor-mations of 4f-i can be rationalised in terms of the pathway shown in Scheme I.3, involving triplet excited states.[2,5]

A benzo-vinyl bridging of the excited state species can lead to the diradical intermediates 7 or 9, which can then be transformed to the regioisomeric products 5 or 6, respectively. Secondary photoreactions involving intramolecular hydrogen abstraction and other transformations lead to products such as 11g and 12h. The exclusive formation of the 4b-substituted semibullvalene, 5f from 4f may be explained in terms of the stabilization of the 'proximal' radical centres in 7 by through space interaction with the hydroxy group. A similar role of the hydroxy group in deciding regioselectivity has been reported in the literature.[23,24]

The 9-ethyl substituted dibenzobarrelene derivative 4g, on irradiation, gave both of the possible regioisomeric semibullvalene derivatives 5g (major) and 6g (minor). However, the 9-benzyl substituted dibenzobarrelene gave the 8b-substituted semibullvalene derived product 12h, exclusively. It has been reported earlier that the irradiation of 9-methyl substituted dibenzobarrelene yielded the 4b-substituted semibullvalene exclusively.[30,31] The electronic effects due to methyl, ethyl and benzyl groups on diradical intermediates such as 7 and 9 are expected to be comparable and hence these results suggest that steric effects have a

role in controlling the regioselectivity in the photo-rearrangement of dibenzobarrelenes.

However, it may be noted that dibenzobarrelenes having bulky bridgehead substituents such as 4i (cyclopentyl), 4j (isopropyl), 4k (cyclohexyl), and 4l (cycloheptyl) exhibit a different photochemistry. These substrates, on irradiation, were converted to the corresponding dibenzocyclo-octatetraenes 16i-l, exclusively, except for 4i, wherein a considerable amount of the 4b-substituted dibenzosemibull-valene 5i was also formed. The formation of the dibenzo-cyclooctatetraenes 16i-l can be rationalised in terms of the pathway shown in Scheme I.4, involving singlet excited states[5-7] and proceeding through quadricyclane intermedia-tes (15).

The formation of a small amount of 20 in the irradia-tion of 4g can be rationalised in terms of the pathway shown in Scheme I.5. The dibenzoylalkene component in 4g can rearrange to the lactones 18 or 20 via the diradical inter-mediates 17 or 19. We assume that the lactone 20, where ethyl and phenyl substituents are farther from each other will be preferentially formed. A similar rearrangement involving the 1,2-dibenzoylalkene component in a bicy-clo[2,2,2]octene system has been reported earlier.[62]

Scheme I.5
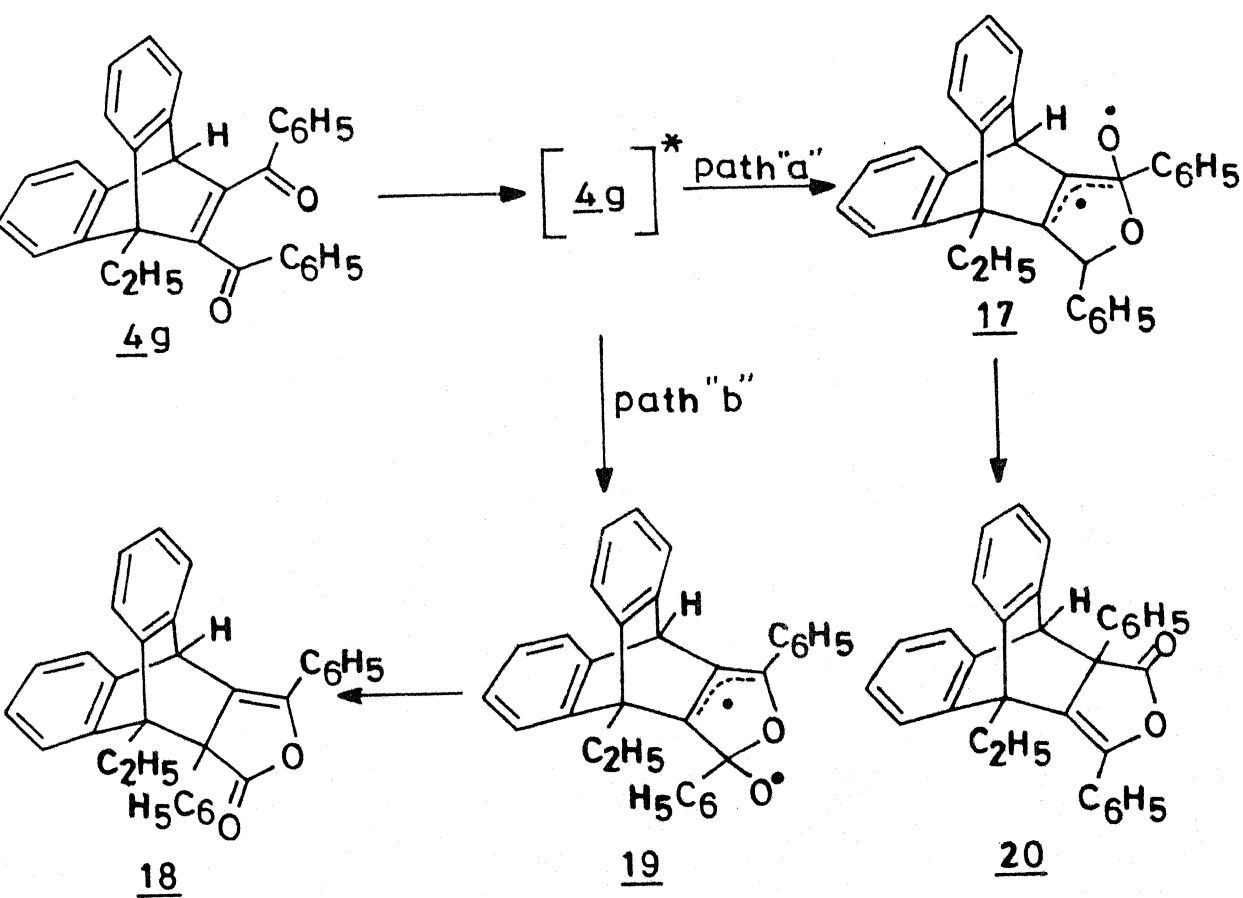
As is evident from the Φ_T data in Table I.1, all the dibenzobarrelenes under examination are characterized by high intersystem crossing efficiencies (close to unity). The diffuse nature of the triplet-triplet absorption spectra of the dibenzobarrelenes (Figure I.5-8) suggests that the triplet excitation involves the barrelene chromophore as a whole, rather than being localized on the dibenzoylalkene moiety. This, combined with the fact that the triplets are short-lived, is taken to mean that the latter can constitute important intermediates in the photochemistry observed under direct irradiation. Interestingly, for 4j and 4k, the triplets are unusually short-lived (Table I.1). These are also the substrates for which, inspite of high Φ_T's, the barrelene-semibullvalene rearrangement does not occur as shown by preparative photochemical studies. It appears that the triplets of these systems undergo fast decay to metastable intermediates, which eventually revert back to the reactants. Based on our results, however, we are unable to ascertain if these intermediates are diradicals 7 or 9 (Scheme I.3) which are reluctant to undergo further transformation to the corresponding semibullvalenes. It should be noted that the triplets of 4e-l may also undergo the Norrish type II photoreaction (intramolecular

γ-hydrogen abstraction) leading to biradicals, which may eventually reketonize to the original reactants.

I.4   EXPERIMENTAL SECTION

All melting points are uncorrected and were determined on a Mel-Temp apparatus.   The IR spectra were recorded on a Perkin-Elmer model 377 infrared spectrometer and the electronic spectra on a Cary 219 spectrophotometer. ^{1}H and ^{13}C NMR traces were recorded on a Varian EM-390 and a Bruker HFX-90 spectrometer, respectively, using tetramethylsilane as internal standard.   The mass spectra were recorded on a Hitachi RMU-6E or a Varian Mat CH7 mass spectrometer at 70 eV.   All steady-state irradiation experiments were carried out in a Srinivasan-Griffin-Rayonet photochemical reactor or using a Hanovia 450 W medium pressure mercury lamp in a quartz-jacketted immersion well with or without pyrex filters.

I.4.1   Starting Materials.   Dibenzoylacetylene (DBA),[63,64] mp 110-111 °C, 9-hydroxymethylanthracene,[65] mp 162-163 °C, 11,12-dibenzoyl-9,10-dihydro-9-hydroxy-9,10-ethenoanthracene (4a),[31] mp 212-213 °C, 11,12-dibenzoyl-9,10-dihydro-9-methoxy-9,10-ethenoanthracene (4b),[32] mp 146 °C, 9-acetoxy-11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracene (4c),[32] mp 232-233 °C, 9-cyano-

11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracene (4d),[32] mp 198 °C, 11,12-dibenzoyl-9,10-dihydro-9-formyl-9,10-etheno-anthracene (4e),[32] mp 191 °C, and 11,12-dibenzoyl-9,10-di-hydro-9-ethyl-9,10-ethenoanthracene (4g),[32] mp 217 °C were prepared by known procedures. 9-Benzylanthracene, mp 135 °C, 9-isopropylanthracene, mp 75-76 °C, 9-cyclopentylanthracene, 9-cyclohexylanthracene, mp 125-126 °C, and 9-cycloheptylan-thracene, mp 114-115 °C were prepared by adaptation of known procedures.[66] Solvents for steady-state irradiation experi-ments were purified and distilled before use. Petroleum ether used was the fraction with bp 60-80 °C. Aldrich Gold-Label solvents were used for laser studies.

I.4.2 Preparation of 11,12-Dibenzoyl-9,10-dihydro-9,10-ethenoanthracenes 4f,h-l. Dibenzobarrelene 4f was prepared by refluxing an equimolar mixture of 9-hydroxy-methylanthracene and DBA in dry toluene for 36 h. Removal of solvent under reduced pressure gave crude 4f as a brown residue, which was washed with chilled methanol and recry-stallized from a mixture (4:1) of benzene and petroleum ether. Dibenzobarrelenes 4h-l were prepared by treating an equimolar mixture of the appropriate anthracene and anhy-drous aluminium chloride with DBA in chloroform at 0 °C. After 1 h, the mixture was poured over crushed ice, acidified

with dilute hydrochloric acid and extracted with chloro-
form. The chloroform layer was separated and dried over
anhydrous magnesium sulphate. Removal of chloroform gave
crude <u>4h-1</u>, which were washed with warm methanol and puri-
fied by recrystallization from a mixture (1:1) of chloro-
form and methanol.

<u>11,12-Dibenzoyl-9,10-dihydro-9-hydroxymethyl-9,10-etheno-
anthracene</u> (<u>4f</u>). <u>4f</u> was obtained in a 88% yield, mp
223-224 $^\circ$C.

IR spectrum ν_{max} (KBr): 3600, 3570 (OH), 3060, 2920,
2880 (CH), 1640 (C=O), 1590 and 1575 (C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 255 nm (ϵ, 19,800) and
322 (1600).

^{1}H NMR spectrum (CDCl$_3$): δ 2.80 (1 H, t, J = 4.5 Hz,
D$_2$O exchangeable, OH), 5.10 (2 H, d, J = 4.5 Hz, CH$_2$),
5.60 (1 H, s, bridgehead), and 7.40 (18 H, m, aromatic).

<u>Anal</u>. Calcd for C$_{31}$H$_{22}$O$_3$: C, 84.16; H, 4.98.
Found: C, 83.88; H, 4.98.

<u>9-Benzyl-11,12-dibenzoyl-9,10-dihydro-9,10-etheno-
anthracene</u> (<u>4h</u>). <u>4h</u> was obtained in a 83% yield, mp 163-
164 $^\circ$C.

IR spectrum ν_{max} (KBr): 3050, 3020, 2980 (CH), 1645
(C=O), 1590 and 1575 (C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 256 nm (ε, 19,400) and 330 (1050).

^{1}H NMR spectrum (CDCl$_3$): δ4.35 (2 H, s, CH$_2$), 5.60 (1 H, s, bridgehead), and 7.25 (23 H, m, aromatic).

<u>Anal</u>. Calcd for C$_{37}$H$_{26}$O$_2$: C, 88.45; H, 5.18. Found: C, 88.92; 4.80.

<u>9-Cyclopentyl-11,12-dibenzoyl-9,10-dihydro-9,10-etheno-anthracene</u> (<u>4i</u>). <u>4i</u> was prepared in a 81% yield, mp 211-212 °C.

IR spectrum ν_{max} (KBr): 3050, 3020, 2920, 2850 (CH), 1640 (C=O), 1590 and 1560 (C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 256 nm (ε, 19,800) and 326 (1100).

^{1}H NMR spectrum (CDCl$_3$): δ2.05 and 3.80 (9 H, m, cyclopentyl), 5.45 (1 H, s, bridgehead), and 7.30 (18 H, m, aromatic).

<u>Anal</u>. Calcd for C$_{35}$H$_{28}$O$_2$: C, 87.50; H, 5.83. Found: C, 87.45; H, 5.78.

<u>11,12-Dibenzoyl-9,10-dihydro-9-isopropyl-9,10-etheno-anthracene</u> (<u>4j</u>). <u>4j</u> was obtained in a 90% yield, mp 180-181 °C.

IR spectrum ν_{max} (KBr): 3050, 2980, 2890 (CH), 1650 (C=O), 1590 and 1570 (C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 256 nm (ϵ, 20,800) and 330 (1300).

^{1}H NMR spectrum (CDCl$_3$): δ 1.35 (3 H, d, CH$_3$), 1.65 (3 H, d, CH$_3$), 3.65 (1 H, m, CH), 5.35 (1 H, s, bridgehead), and 7.38 (18 H, m, aromatic).

<u>Anal</u>. Calcd for C$_{33}$H$_{26}$O$_2$: C, 87.22; H, 5.73. Found: C, 87.15; H, 5.58.

<u>9-Cyclohexyl-11,12-dibenzoyl-9,10-dihydro-9,10-etheno-anthracene (4k)</u>. <u>4k</u> was isolated in a 92% yield, mp 219-220 °C.

IR spectrum ν_{max} (KBr): 3060, 3020, 2930, 2850 (CH), 1635 (C=O), 1580 and 1560 (C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 256 nm (ϵ, 20,000) and 327 (1500).

^{1}H NMR spectrum (CDCl$_3$): δ 1.90 and 3.30 (11 H, m, cyclohexyl), 5.35 (1 H, s, bridgehead), and 7.45 (18 H, m, aromatic).

<u>Anal</u>. Calcd for C$_{36}$H$_{30}$O$_2$: C, 87.45; H, 6.07. Found: C, 87.20; H, 5.95.

9-Cycloheptyl-11,12-dibenzoyl-9,10-dihydro-9,10-etheno-
anthracene (4k). 4k was obtained in a 86% yield, mp 194-
195 °C.

IR spectrum ν_{max} (KBr): 3080, 3060, 3030, 2960, 2940,
2920, 2850 (CH), 1650 (C=O), 1590 and 1560 (C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 256 nm (ε, 19,800) and
326 (1400).

^{1}H NMR spectrum (CDCl$_3$): δ1.50 and 3.50 (13 H, m,
cycloheptyl), 5.35 (1 H, s, bridgehead), and 7.40 (18 H, m,
aromatic).

Anal. Calcd for C$_{37}$H$_{32}$O$_2$: C, 87.40; H, 6.30. Found: C,
87.13; H, 6.06.

I.4.3 Irradiation of 11,12-Dibenzoyl-9,10-dihydro-
9-hydroxymethyl-9,10-ethenoanthracene (4f). A solution of
4f (442 mg, 1 mmol) in benzene (175 mL) was irradiated using
a Hanovia 450 W medium pressure mercury vapour lamp for
1/4 h. Removal of the solvent gave a residue, which was
triturated with carbon tetrachloride to separate 285 mg (64%)
of 5f, mp 190-191 °C, after recrystallization from a mixture
(4:1) of benzene and petroleum ether.

IR spectrum ν_{max} (KBr): 3470, 3320 (OH), 3060, 3025,
2960, 2920 (CH), 1650 (C=O), 1590 and 1580 (C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 221 nm (ε, 34,400, sh), 248 (24,800), and 284 (5100).

^{13}C NMR spectrum (CDCl$_3$): δ 48.37 (C-8b), 59.53 (CH$_2$), 61.67 (C-4b), 119.9-150.11 (aromatic), and 195.27 and 197.00 (C=O).

Mass spectrum, m/e (relative intensity): 440 (M$^+$, 10), 410 (M$^+$- CH$_2$O, 36), 335 (M$^+$- C$_6$H$_5$CO, 2), 318 (M$^+$- C$_6$H$_5$CO, - OH, 7), 305 (M$^+$- C$_6$H$_5$CO, - CH$_2$O, 10), 105 (C$_6$H$_5$CO$^+$, 100), and other peaks.

<u>Anal</u>. Calcd for C$_{31}$H$_{22}$O$_3$: C, 84.16; H, 4.98. Found: C, 84.10; H, 5.25.

In a repeat run, a methanol solution of <u>4f</u> (442 mg, 1 mmol in 175 mL) was irradiated and worked up under identical conditions to separate 365 mg (83%) of <u>5f</u>, mp 190-191 ^{o}C (mixture melting point).

In yet another run, a solution of <u>4f</u> (442 mg, 1 mmol) in acetone (175 mL) was irradiated and worked up as in the earlier cases to separate 350 mg (79%) of <u>5f</u>, mp 190-191 ^{o}C (mixture melting point).

I.4.4 <u>Irradiation of 11,12-Dibenzoyl-9,10-dihydro-9-ethyl-9,10-ethenoanthracene</u> (<u>4g</u>).[32] A solution of <u>4g</u> (880 mg, 2 mmol) in benzene (175 mL) was irradiated using a

Hanovia 450 W medium pressure mercury vapour lamp for 1 h. The solvent was removed under reduced pressure and the resultant residue was chromatographed over silica gel. Elution with a mixture (2:3) of benzene and petroleum ether gave 545 mg (62%) of 5g, mp 192-193 $^{\circ}$C (lit.[32] mp 192 $^{\circ}$C), after recrystallization from a mixture (2:3) of benzene and petroleum ether. Further elution with a mixture (1:1) of benzene and petroleum ether gave 25 mg (3%) of the unchanged 4g, mp 216-217 $^{\circ}$C (mixture melting point). Continued elution with a mixture (7:3) of benzene and petroleum ether gave 160 mg (18%) of the isomeric hydroxy compound 11g, mp 175 $^{\circ}$C (dec.), after recrystallization from a mixture (1:1) of chloroform and methanol.

IR spectrum ν_{max} (KBr): 3500 (OH), 3050, 3020, 2960 (CH), and 1590 (C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 218 nm (ϵ, 29,300, sh), 244 (28,600), and 272 (5800, sh).

Anal. Calcd for C$_{32}$H$_{24}$O$_2$: C, 87.26; H, 5.45. Found: C, 86.93; H, 5.65.

In a repeat run, irradiation of a methanol solution of 4g (880 mg, 2 mmol in 175 mL) under analogous conditions, followed by workup in the usual manner gave 600 mg (68%) of 5g, mp 192-193 $^{\circ}$C (mixture melting point), 115 mg (13%) of

11g, mp 175 °C (dec., mixture melting point) and 25 mg (3%) of the unchanged 4g, mp 216-217 °C (mixture melting point).

In another run, a solution of 4g (830 mg, 1 mmol) in acetone (175 mL) was irradiated and worked up as in the earlier cases to separate 555 mg (63%) of 5g, mp 192-193 °C (mixture melting point), 165 mg (19%) of 11g, mp 175 °C (dec., mixture melting point), 25 mg (3%) of the unchanged 4g, mp 216-217 °C (mixture melting point) and 20 mg (2%) of an isomeric lactone 20, mp 171-172 °C (elution with a mixture (1:4) of benzene and petroleum ether and recrystallization from methanol).

IR spectrum ν_{max} (KBr): 3060, 2980, 2920 (CH), 1750 (C=O), 1645 and 1590 (C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 236 nm (ε, 7700), 265 (2500, sh), 272 (2100, sh), and 279 (1700, sh).

Mass spectrum, m/e (relative intensity): 440 (M$^+$, 19), 412 (M$^+$ - CO, 1), 411 (M$^+$ - C$_2$H$_5$, 11), 363 (M$^+$ - C$_6$H$_5$, 100), 335 (M$^+$ - C$_6$H$_5$CO, 47), 105 (C$_6$H$_5$CO$^+$, 100), and other peaks.

Anal. Calcd for C$_{32}$H$_{24}$O$_2$: C, 87.26; H, 5.45. Found: C, 87.20; H, 5.74.

I.4.5 Irradiation of 9-Benzyl-11,12-dibenzoyl-9,10-di-hydro-9,10-ethenoanthracene (4h). A benzene solution of 4h

(502 mg, 1 mmol in 150 mL) was irradiated for 3 h (RPR, 350 nm). After removal of the solvent under reduced pressure, the residue was chromatographed over silica gel. Elution with a mixture (3:7) of benzene and petroleum ether gave 110 mg (22%) of 9-benzylidene-9a,10-dibenzoyl-4b,9,9a,10-tetrahydro-cis-indeno[1,2-a]indene (12h), mp 222 °C, after recrystallization from a mixture (1:1) of chloroform and methanol.

IR spectrum ν_{max} (KBr): 3050, 3010, 2960 (CH), 1665 (C=O), 1590 and 1570 (C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 244 nm (ε, 32,700), 274 (12,900), 283 (11,300, sh), and 292 (10,200, sh).

^{1}H NMR spectrum (CDCl$_3$): δ 5.65 (1 H, s, H-4b), 6.29 (1 H, s, H-10), and 7.40 (24 H, m, aromatic and benzylidenic).

^{13}C NMR spectrum (CDCl$_3$): δ 56.22 (C-10), 61.32 (C-4b), 73.32 (C-9a), 123.76-148.80 (aromatic and vinylic), and 198.88 and 199.14 (C=O).

Mass spectrum, m/e (relative intensity): 502 (M$^+$, 15), 397 (M$^+$ - C$_6$H$_5$CO, 17), 105 (C$_6$H$_5$CO$^+$, 100), and other peaks.

Anal. Calcd for C$_{37}$H$_{26}$O$_2$: C, 88.45; H, 5.18. Found: C, 88.36; H, 5.22.

Further elution with a mixture (1:1) of benzene and petroleum ether gave 210 mg (42%) of the unchanged 4h, mp 163-164 °C (mixture melting point).

In a repeat run, a methanol solution of 4h (502 mg, 1 mmol in 150 mL) was irradiated and worked up as in the earlier cases to separate 105 mg (21%) of 12h, mp 222 °C (mixture melting point) and 280 mg (56%) of the unchanged 4h, mp 163-164 °C (mixture melting point).

In yet another run, a solution of 4h (502 mg, 1 mmol) in acetone (150 mL) was irradiated for 2 h (RPR, 253.7 nm). Workup as in the earlier cases yielded 90 mg (18%) of 12h, mp 222 °C (mixture melting point) and 265 mg (53%) of the unchanged 4h, mp 163-164 °C (mixture melting point).

I.4.6 Irradiation of 9-Cyclopentyl-11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracene (4i). A benzene solution of 4i (480 mg, 1 mmol in 150 mL) was irradiated for 2 h (RPR, 350 nm). The solvent was removed under reduced pressure and the resultant residue was chromatographed over silica gel. Elution with a mixture (2:3) of benzene and petroleum ether gave 95 mg (20%) of the unchanged 4i, mp 211-212 °C (mixture melting point). Further elution with a mixture (1:1) of

benzene and petroleum ether gave a mixture of the dibenzo-
semibullvalene 5i and the dibenzocyclooctatetraene 16i,
which were separated by fractional crystallization from a
mixture (1:1) of chloroform and methanol. The fraction
that separated out first was identified as 16i (115 mg,
25%), mp 188-189 °C, after recrystallization from a mix-
ture (1:1) of benzene and petroleum ether.

IR spectrum ν_{max} (KBr): 3050, 3020, 2910, 2840 (CH),
1650 (C=O), 1590 and 1570 (C=C) cm^{-1}.

UV spectrum λ_{max} (CH_3OH): 248 nm (ε, 27,800) and
286 (9300, sh).

^{1}H NMR spectrum ($CDCl_3$): δ 1.90 (9 H, m, cyclopentyl),
and 7.70 (19 H, m, aromatic and vinylic).

Mass spectrum, m/e (relative intensity): 480 (M^+, 80),
412 ($M^+ - C_5H_8$, 20), 375 ($M^+ - C_6H_5CO$, 85), 307 ($M^+ -
C_6H_5CO$, $- C_5H_8$, 77), 105 ($C_5H_5CO^+$, 100), and other peaks.

<u>Anal</u>. Calcd for $C_{35}H_{28}O_2$: C, 87.50; H, 5.83. Found: C,
87.85; H, 5.91.

The mother liquor, after the separation of 16i, was
concentrated to isolate 85 mg (18%) of 5i, mp 170-171 °C,
after recrystallization from a mixture (1:1) of benzene and
petroleum ether.

IR spectrum ν_{max} (KBr): 3050, 3010, 2920, 2840 (CH), 1660 (C=O), 1590 and 1580 (C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 221 nm (ε, 32,000, sh) and 255 (23,100).

^{1}H NMR spectrum (CDCl$_3$): δ 1.55 and 3.30 (9 H, m, cyclopentyl), 4.7 (1 H, s, H-8b), and 7.40 (18 H, m, aromatic).

Anal. Calcd for C$_{35}$H$_{28}$O$_2$: C, 87.50; H, 5.83. Found: C, 87.15; H, 6.05.

In a repeat run, the irradiation of a solution of 4i (480 mg, 1 mmol) in methanol (150 mL), followed by workup under analogous conditions, gave 95 mg (20%) of the unchanged 4i, mp 211-212 °C (mixture melting point), 100 mg (21%) of 5i, mp 170-171 °C (mixture melting point), and 110 mg (23%) of 16i, mp 188-189 °C (mixture melting point).

In another run, an acetone solution of 4i (480 mg, 1 mmol in 150 mL) was irradiated for 2 h (RPR, 253.7 nm). Workup as in the earlier cases yielded 95 mg (20%) of the unchanged 4i, mp 211-212 °C (mixture melting point), 110 mg (23%) of 5i, mp 170-171 °C (mixture melting point) and 100 mg (21%) of 16i, mp 188-189 °C (mixture melting point).

I.4.7 <u>Irradiation of 11,12-Dibenzoyl-9,10-dihydro-</u>
<u>9-isopropyl-9,10-ethenoanthracene</u> (<u>4j</u>). A solution of <u>4j</u>
(454 mg, 1 mmol) in benzene (150 mL) was irradiated for 3 h
(RPR, 350 nm). The photolysate, after removal of the sol-
vent under reduced pressure, was chromatographed over silica
gel. Elution with a mixture (2:3) of benzene and petroleum
ether gave 215 mg (45%) of the unchanged <u>4j</u>, mp 180-181 °C
(mixture melting point). Further elution with a mixture
(1:1) of benzene and petroleum ether gave 100 mg (22%) of
the dibenzocyclooctatetraene <u>16j</u>, mp 149-150 °C, after
recrystallization from a mixture (1:1) of chloroform and
methanol.

IR spectrum ν_{max} (KBr): 3060, 2960, 2920 (CH), 1660
(C=O), 1590 and 1575 (C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 248 nm (ε, 28,800) and
280 (10,900, sh).

^{1}H NMR spectrum (CDCl$_3$): δ 0.85 (3 H, d, CH$_3$), 0.95
(3 H, d, CH$_3$), 3.5 (1 H, m, CH), 5.8 (1 H, s, vinylic) and
7.50 (18 H, m, aromatic).

^{13}C NMR spectrum (CDCl$_3$): δ 21.75 (CH$_3$), 34.00 (CH),
126.00-148.14 (aromatic and vinylic), and 195.80 and 197.68
(C=O).

Mass spectrum, m/e (relative intensity): 454 (M^+, 7), 411 (M^+ - $CH(CH_3)_2$, 9), 349 (M^+ - C_6H_5CO, 8), 348 (M^+ - C_6H_5CO, - H, 10), 306 (M^+ - C_6H_5CO, - $CH(CH_3)_2$, 10), 105 ($C_6H_5CO^+$, 100), and other peaks.

<u>Anal</u>. Calcd for $C_{33}H_{26}O_2$: C, 87.22; H, 5.73. Found: C, 87.05; H, 5.58.

In a repeat run, a methanol solution of <u>4j</u> (454 mg, 1 mmol in 150 mL) was irradiated under analogous conditions and worked up as in the earlier cases to give 220 mg (48%) of the unchanged <u>4j</u>, mp 180-181 $^{\circ}$C (mixture melting point) and 95 mg (21%) of <u>16j</u>, mp 149-150 $^{\circ}$C (mixture melting point).

In yet another run, a solution of <u>4j</u> (454 mg, 1 mmol) in acetone (150 mL) was irradiated for 2 h (RPR, 253.7 nm). Workup as in the earlier cases gave 230 mg (51%) of the unchanged <u>4j</u>, mp 180-181 $^{\circ}$C (mixture melting point) and 95 mg (21%) of <u>16j</u>, mp 149-150 $^{\circ}$C (mixture melting point).

I.4.8 <u>Irradiation of 9-Cyclohexyl-11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracene</u> (<u>4k</u>). A solution of <u>4k</u> (494 mg, 1 mmol) in benzene (150 mL) was irradiated for 4 h (RPR, 300 nm). After removal of the solvent under reduced pressure, the residue was chromatographed over silica gel.

Elution with a mixture (2:3) of benzene and petroleum ether gave 105 mg (21%) of the unchanged 4k, mp 219-220 $^{\circ}$C (mixture melting point). Further elution with a mixture (1:1) of benzene and petroleum ether gave 270 mg (55%) of the dibenzocyclooctatetraene 16k, mp 228-229 $^{\circ}$C, after recrystallization from a mixture (1:1) of chloroform and methanol.

IR spectrum ν_{max} (KBr): 3060, 3020, 2920, 2840 (CH), 1650 (C=O), 1590 and 1575 (C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 248 nm (ε, 25,900) and 275 (9400, sh).

^{1}H NMR spectrum (CDCl$_3$): δ 1.70 (11 H, m, cyclohexyl) and 7.75 (19 H, m, aromatic and vinylic).

^{13}C NMR spectrum (CDCl$_3$): δ 25.37, 26.10, 31.65, 31.87 and 45.06 (cyclohexyl), 126.35-148.59 (aromatic and vinylic), and 195.79 and 197.77 (C=O).

Mass spectrum, m/e (relative intensity): 494 (M$^+$, 9), 412 (M$^+$ - C$_6$H$_{10}$, 4), 389 (M$^+$ - C$_6$H$_5$CO, 6), 307 (M$^+$ - C$_6$H$_5$CO, - C$_6$H$_{10}$, 15), 105 (C$_6$H$_5$CO$^+$, 100), and other peaks.

Anal. Calcd for C$_{36}$H$_{30}$O$_2$: C, 87.45; H, 6.07. Found: C, 87.11; H, 6.41.

In a repeat run, a solution of 4k (494 mg, 1 mmol) in methanol (150 mL) was irradiated for 4 h and worked up as

in the earlier cases to give 80 mg (16%) of the unchanged 4k, mp 219-220 °C (mixture melting point) and 225 mg (46%) of 16k, mp 228-229 °C (mixture melting point).

In another run, a solution of 4k (494 mg, 1 mmol) in acetone (150 mL) was irradiated for 3 h (RPR, 253.7 nm) and worked up to give 80 mg (16%) of the unchanged 4k, mp 219-220 °C (mixture melting point) and 225 mg (46%) of 16k, mp 228-229 °C (mixture melting point).

I.4.9 Irradiation of 9-Cycloheptyl-11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracene (41). A solution of 41 (100 mg, 0.2 mmol) in benzene (150 mL) was irradiated for 5 h (RPR, 350 nm). Removal of the solvent under vacuum and recrystallization of the resultant residue from a mixture (1:1) of chloroform and methanol gave 88 mg (88%) of 161, mp 197-198 °C.

IR spectrum ν_{max} (KBr): 3040, 3020, 2900, 2840 (CH), 1650 (C=O), 1580 and 1550 (C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 248 nm (ε, 25,400) and 277 (9600, sh).

^{1}H NMR spectrum (CDCl$_3$): δ 1.85 (13 H, m, cycloheptyl) and 7.60 (19 H, m, aromatic and vinylic).

Anal. Calcd for C$_{37}$H$_{32}$O$_2$: C, 87.40; H, 6.30. Found: C, 87.13; H, 6.21.

In a repeat run, a methanol solution of 41 (100 mg, 0.2 mmol in 150 mL) was irradiated for 5 h (RPR, 350 nm). Removal of the solvent under vacuum gave a product mixture, which was separated by preparative thin layer chromatography over silica gel to give 20 mg (20%) of the unchanged 41, mp 211-212 $^{\circ}$C (mixture melting point) and 70 mg (70%) of 161, mp 197-198 $^{\circ}$C (mixture melting point).

I.4.10   Attempted Triplet Sensitized Irradiations of the Dibenzobarrelenes 4i-1.   Benzene solutions of 4i-1 (2.2 mM) were irradiated separately, in the presence of excess of biacetyl (22 mM) as sensitizer for 1/4-1/2 h, using the output from a Hanovia 450 W medium pressure mercury vapour lamp, selectively filtered through a pyrex glass sleeve (1 mm thick) and a 0.02% (w/v) solution of 9,10-dibromoanthracene in toluene (path length, 1 cm). Workup of the mixture in the usual manner gave unchanged 4i-1 (87-92%).

I.4.11   Ozonolysis of 9-Benzylidene-9a,10-dibenzoyl-4b,9,9a,10-tetrahydro-cis-indeno[1,2-a]indene (12h).   A solution of 12h (250 mg, 0.5 mmol) in methanol (50 mL) was ozonized at 0 $^{\circ}$C. The reaction mixture was treated with excess of alkaline hydrogen peroxide, poured into water and

extracted with chloroform. Removal of the solvent under vacuum gave a residue, which was triturated with methanol and recrystallized from a mixture (1:1) of benzene and petroleum ether to give 125 mg (57%) of 13, mp 208-209 ^{o}C[31] (mixture melting point). Acidification of the aqueous layer gave 30 mg (50%) of benzoic acid (14), mp 121-122 ^{o}C (mixture melting point), after recrystallization from water.

I.4.12 <u>Laser Flash Photolysis</u>.[53] The laser flash photolysis studies were performed mostly with 337.1 nm laser pulses (8 ns, 2-3 mJ) from a Molectron UV-400 nitrogen laser system. For some experiments, outputs at 485 and 532 nm (6 ns, 5-10 mJ) from a Quanta-Ray Nd-Yag DCR-1 source coupled with Quanta-Ray PDL-1 dye laser were also used. The details of the kinetic spectrophotometer and data collection system are given elsewhere.[67,68]

I.4.13 <u>Pulse Radiolysis</u>.[53] The pulse radiolysis experiments were performed, employing 7-MeV electron pulses (5 ns) from the Notre Dame ARCO-LP-7 linear accelerator in the computer controlled apparatus, described elsewhere.[69,70]

I.5 <u>REFERENCES</u>

(1) H. E. Zimmerman and G. L. Grunewald, J. Am. Chem. Soc.,
     <u>88</u>, 183 (1966).

(2) H. E. Zimmerman and P. S. Mariano, J. Am. Chem. Soc.,
     <u>91</u>, 1718 (1969).

(3) S. S. Hixson, P. S. Mariano and H. E. Zimmerman,
     Chem. Rev., <u>73</u>, 541 (1973).

(4) H. E. Zimmerman, "Rearrangements in Ground and Excited
     States" P. de Mayo, Ed. , Academic Press, New York,
     Vol. 3, P. 131 (1980).

(5) H. E. Zimmerman, R. W. Binkley, R. S. Givens and
     M. A. Sherwin, J. Am. Chem. Soc., <u>89</u>, 3932 (1967).

(6) H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L.
     Grunewald and M. A. Sherwin, J. Am. Chem. Soc., <u>91</u>,
     3316 (1969).

(7) P. W. Rabideau, J. B. Hamilton and L. Friedman,
     J. Am. Chem. Soc., <u>90</u>, 4465 (1968).

(8) J. P. N. Brewer and H. Heaney, Chem. Commun., 811 (1967).

(9) R. S. H. Liu, J. Am. Chem. Soc., <u>90</u>, 215 (1968).

(10) H. E. Zimmerman, R. S. Givens and R. M. Pagni, J. Am.
     Chem. Soc., <u>90</u>, 4191 (1968).

(11) H. E. Zimmerman, R. S. Givens and R. M. Pagni, J. Am. Chem. Soc., 90, 6096 (1968).

(12) R. S. Givens and W. F. Oettle, Chem. Commun., 1066 (1969).

(13) C. O. Bender and S. S. Sugarman, Chem. Commun., 934 (1974).

(14) C. O. Bender and D. W. Brooks, Can. J. Chem., 53, 1684 (1975).

(15) C. O. Bender and E. H. King-Brown, Chem. Commun., 878 (1976).

(16) C. O. Bender and J. Wilson, Helv. Chim. Acta, 59, 1469 (1976).

(17) H. E. Zimmerman and C. O. Bender, J. Am. Chem. Soc., 91, 7516 (1969).

(18) H. E. Zimmerman and C. O. Bender, J. Am. Chem. Soc., 92, 4366 (1970).

(19) C. O. Bender, J. L. M. Elder, A. J. Herbst and L. E. Miller, Can. J. Chem., 50, 395 (1972).

(20) C. O. Bender and H. O. Burgess, Can. J. Chem., 51, 3486 (1973).

(21) H. E. Zimmerman and M. -L. Viriot-Villaume, J. Am. Chem. Soc., 95, 1274 (1973).

(22) E. Ciganek, J. Am. Chem. Soc., 88, 2882 (1966).

(23) H. Hart and R. K. Murray, Jr., J. Am. Chem. Soc., 91, 2183 (1969).

(24) H. Hart and G. M. Love, J. Am. Chem. Soc., 95, 4592 (1973).

(25) K. E. Richards, R. W. Tillman and G. J. Wright, Aust. J. Chem., 28, 1289 (1975).

(26) R. G. Paddick, K. E. Richards and G. J. Wright, Aust. J. Chem., 29, 1005 (1976).

(27) L. A. Paquette and E. Bay, J. Am. Chem. Soc., 106, 6693 (1984).

(28) M. Iwamura, H. Tukada and H. Iwamura, Tetrahedron Lett., 4865 (1980).

(29) S. Lahiri, Ph.D. Thesis, Indian Institute of Technology, Kanpur, India (1977).

(30) C. V. Kumar, B. A. R. C. Murty, S. Lahiri, E. Chackachery, J. C. Scaiano and M. V. George, J. Org. Chem., 49, 4923 (1984).

(31) C. V. Kumar, Ph. D. Thesis, Indian Institute of Technology, Kanpur, India (1981).

(32) B. A. R. C. Murty, Ph. D. Thesis, Indian Institute of Technology, Kanpur, India (1982).

(33) H. E. Zimmerman and D. R. Amick, J. Am. Chem. Soc., 95, 3977 (1973).

(34) H. E. Zimmerman, D. R. Amick and H. Hemetsberger, J. Am. Chem. Soc., 95, 4606 (1973).

(35) R. S. Givens and W. F. Oettle, Chem. Commun., 1164 (1969).

(36) R. K. Murray, Jr. and H. Hart, Tetrahedron Lett., 4995 (1968).

(37) H. Hart, R. K. Murray, Jr. and G. L. Appleyard, Tetrahedron Lett., 4785 (1969).

(38) H. D. Becker and B. Ruge, Angew. Chem. Int. Ed. Engl., 14, 761 (1975).

(39) H. Hart and R. K. Murray, Jr., Tetrahedron Lett., 215 (1969).

(40) J. Ipaktschi, Tetrahedron Lett., 215 (1969).

(41) L. A. Paquette and R. H. Meisinger, Tetrahedron Lett., 1479 (1970).

(42) R. S. Givens and W. F. Oettle, J. Am. Chem. Soc., 93, 3963 (1971).

(43) R. S. Givens, W. F. Oettle, R. L. Coffin and R. G. Carlson, J. Am. Chem. Soc., 93, 3957 (1971).

(44) M. Kuzuya, E. Mano, M. Ishikawa, T. Okuda and H. Hart, Tetrahedron Lett., 1613 (1981).

(45)   M. Demuth, C. O. Bender, S. E. Braslavsky, H. Gorner,
       U. Bürger, W. Amerin and K. Schaffner, Helv. Chim.
       Acta, 62, 847 (1979).

(46)   M. Demuth, W. Amerein, C. O. Bender, S. E. Braslavsky,
       U. Bürger, M. V. George, D. Lemmer and K. Schaffner,
       Tetrahedron, 37, 3245 (1981).

(47)   H. Hemetsberger, W. Bräuer and D. Tartler, Chem. Ber.,
       110, 1586 (1977).

(48)   H. E. Zimmerman, R. J. Boettcher, N. E. Buehler,
       G. E. Keck and M. G. Steinmetz, J. Am. Chem. Soc.,
       98, 7680 (1976).

(49)   For pertinent references on the photorearrangement of
       1,2-dibenzoylalkenes, see Chapter II of this thesis.

(50)   D. M. McKinnon and J. Y. Wong, Can. J. Chem., 49,
       3178 (1971).

(51)   C. F. Willcox and M. P. Stevens, J. Am. Chem. Soc.,
       84, 1258 (1962).

(52)   J. G. Calvert and J. N. Pitts, "Photochemistry",
       Wiley, New York, P. 738 (1966).

(53)   All laser flash photolysis and pulse radiolysis
       studies were carried out by Dr. P. K. Das, Mr. D. R.
       Cyr and Professor M. V. George at the Radiation
       Laboratory of the University of Notre Dame, U. S. A.

(64) R. E. Lutz and W. R. Smithey, Jr., J. Org. Chem., 16, 51 (1951).

(65) F. H. C. Stewart, Aust. J. Chem., 13, 478 (1960).

(66) J. S. Meek, P. A. Monroe and C. J. Boublis, J. Org. Chem., 28, 2572 (1963).

(67) P. K. Das, M. V. Encinas, R. D. Small, Jr. and J. C. Scaiano, J. Am. Chem. Soc., 101, 6965 (1979) and references therein.

(68) V. Nagarajan and R. W. Fessenden, J. Phys. Chem., 89, 2330 (1985).

(69) L. K. Patterson and J. Lilie, Int. J. Radiat. Phys. Chem., 6, 129 (1974).

(70) R. H. Schuler, Chem. Ed., 2, 34 (1985).

CHAPTER II

PHOTOCHEMICAL TRANSFORMATIONS OF A FEW
(E)-1-(2-ARYLIDENE-1-PHENYLHYDRAZINYL)-1,2-DIBENZOYL-
ETHYLENES

II.1 ABSTRACT

The photochemistry of several (E)-1-(2-arylidene-1-phenylhydrazinyl)-1,2-dibenzoylethylenes such as (E)-1-(2-benzylidene-1-phenylhydrazinyl)-1,2-dibenzoyl-ethylene (12a), (E)-1-(2-p-methylbenzylidene-1-phenyl-hydrazinyl)-1,2-dibenzoylethylene (12b), (E)-1-(2-p-methoxy-benzylidene-1-phenylhydrazinyl)-1,2-dibenzoylethylene (12c), (E)-1-(2-p-cyanobenzylidene-1-phenylhydrazinyl)-1,2-diben-zoylethylene (12d), (E)-1-(2-p-acetoxybenzylidene-1-phenyl-hydrazinyl)-1,2-dibenzoylethylene (12e), (E)-1-(2-p-carbo-methoxybenzylidene-1-phenylhydrazinyl)-1,2-dibenzoylethylene (12f), (E)-1-(2-p-dimethylaminobenzylidene-1-phenylhydra-zinyl)-1,2-dibenzoylethylene (12g), and (E)-1-(2-p-chloro-benzylidene-1-phenylhydrazinyl)-1,2-dibenzoylethylene (12h) has been examined by steady-state irradiation, product ana-lysis and laser flash photolysis. The 1,2-dibenzoylethy-lenes 12a-h have been prepared by the addition of the

corresponding benzaldehyde phenylhydrazones 9a-h to dibenzoylacetylene (DBA, 10).

Irradiation of 12a-h in solvents such as benzene and methanol gave the corresponding 3-aryl-4,5-dibenzoyl-1-phenyl-pyrazoles 18a-h in good yields, along with small amounts of 1-anilino-1,2-dibenzoylethylene (19) and the unchanged 12a-h. The formation of pyrazoles 18a-h in these reactions can be understood in terms of photochemical electrocyclic ring closure reactions, leading to zwitterionic intermediates 13a-h, which subsequently undergo intramolecular hydrogen shifts to give the corresponding pyrazolines 14a-h. Subsequent air oxidation of these pyrazolines will lead to the pyrazoles 18a-h. The formation of small amounts of 19 in these reactions can be understood in terms of photofragmentation reactions, resulting in N-N bond cleavage, followed by hydrogen atom abstraction reactions.

The transient absorption spectral changes from direct laser excitation, as well as under triplet sensitization are explained in terms of the formation of zwitterionic intermediates 13a-h and in part, by cis-trans isomerization of the ethylenic double bond. The triplets of 12a-h are not observed on the nanosecond time scale, presumably because of their short lifetimes.

II.2 INTRODUCTION

1,2-Dibenzoylalkenes are known to undergo interesting photorearrangements leading to ketene derived products, besides cis-trans isomerization.[1-5] Thus, it has been reported that the irradiation of cis-dibenzoylstilbene (1) in a mixture (1:1) of benzene and methanol, for example, gives a mixture of methyl 4-phenoxy-3,4,5-triphenyl-3-butenoate (4b) and trans-dibenzoylstilbene (3).[4] Similar transformations have been observed in the case of dibenzoylstyrene, 1,2-dibenzoylethylene and related dibenzoylalkenes. Padwa et al.[3] have shown that the photolysis of trans-dibenzoylstilbene (3) gives rise to different products, depending on the solvent employed. Thus, the photolysis of 3 in dry benzene, for example, gave a mixture of cis-dibenzoylstilbene (1) and 1-hydroxy-2,3-diphenyl-4-phenoxy-naphthalene (6), whereas 4-phenoxy-2,3,4-triphenyl-3-butenoic acid (4a) was formed in aqueous dioxane. The formation of the different products in such reactions has been rationalized in terms of the pathway shown in Scheme II.1.[3,4]

Recent studies from this laboratory have shown that the irradiation of cis-1,2-dibenzoylalkenes, wherein the cis-trans isomerization is restricted due to structural

Scheme II.1

1 → hν → [**1**]* → **2**

1 ⇌ **3**

4 a) R = H
  b) R = CH₃

5
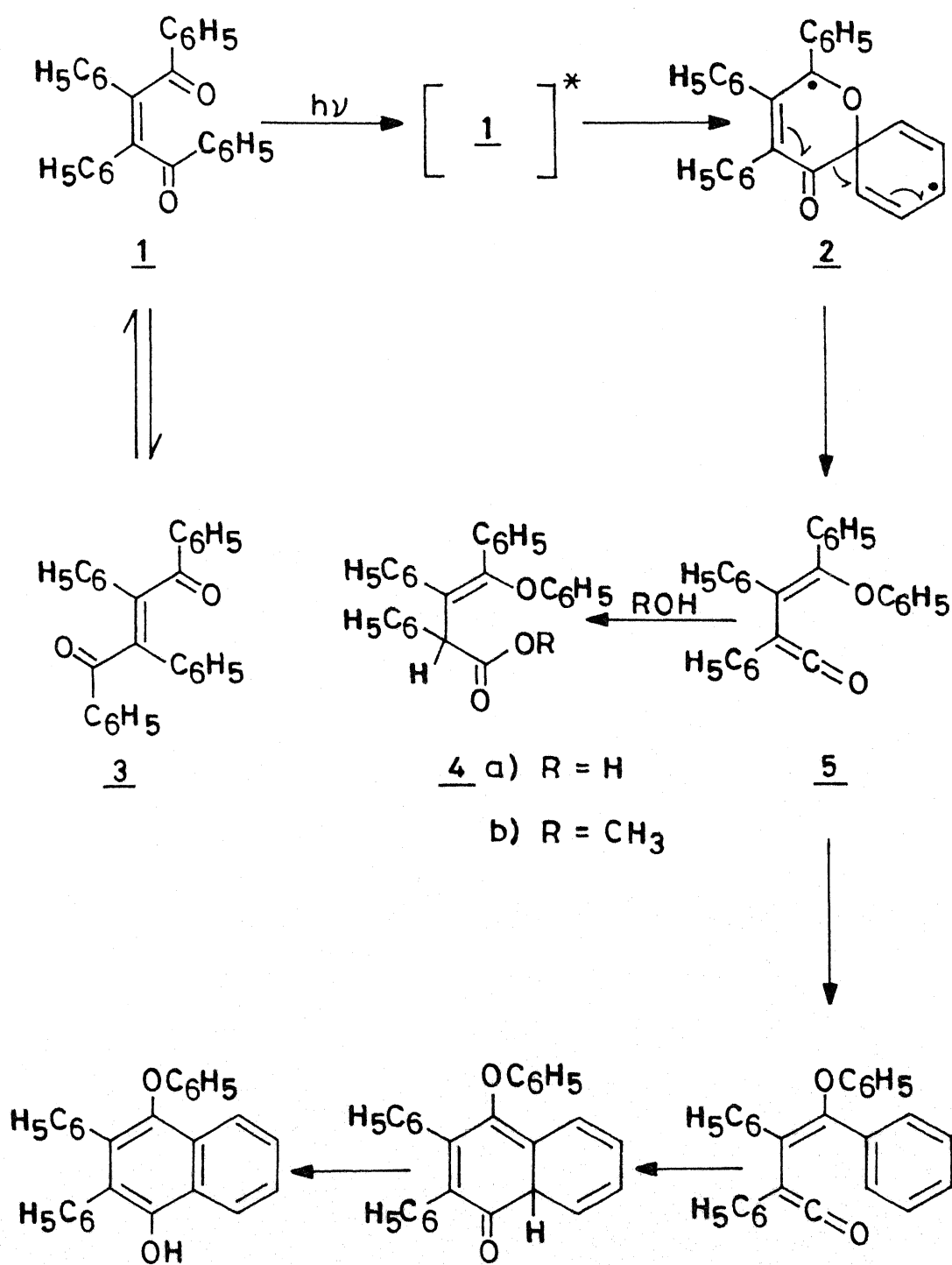
constraints, gives rise to ketene-derived products pre-dominantly.[6] Also, it has been shown that the photo-transformations of 1,2-dibenzoylalkenes are strongly influenced by the nature of the substituents present in them.[7-18] Thus, dibenzobarrelenes containing 1,2-diben-zoylalkene moieties have been found to undergo reactions characteristic of barrelene chromophore,[9-12,19] whereas, 1-imidazolyl and 1-pyrazolyl-1,2-dibenzoylalkenes undergo the dibenzoylalkene rearrangement, as well as electro-cyclic reactions involving aryl substituents present on the imidazolyl and pyrazolyl rings.[13-16] In contrast to these, 1-aziridinyl-1,2-dibenzoylalkenes have been found to undergo facile ring-expansion reactions leading to pyrazoline derivatives and photofragmentation rea-ctions.[16,17]

In some preliminary studies, we had shown earlier[20] that (E)-1-(2-arylidene-1-phenylhydrazinyl)-1,2-dibenzoyl-ethylenes such as 12a,c undergo photocyclization, leading to the corresponding 3-aryl-4,5-dibenzoyl-1-phenylpyra-zoles. A close examination of the structural features of 12a,c reveals that these substrates, in principle, should be capable of undergoing dibenzoylalkene rearrangement, leading to ketene derived products[1-5] and also the

pentadienyl anion mode of cyclization,[21-25] leading to pyrazoline derivatives. It would be expected that such cyclization reactions are symmetry allowed both under photochemical and thermal conditions.[26] In this context, it was felt necessary to examine the photochemistry of some representative ($\underline{E}$)-1-(2-arylidene-1-phenylhydra-zinyl)-1,2-dibenzoylethylenes to study the nature of products formed in these reactions and also the mechanistic details. In the present studies, we have examined the photochemistry of several ($\underline{E}$)-1-(2-arylidene-1-phenyl-hydrazinyl)-1,2-dibenzoylethylenes to study the mode of reaction followed by these substrates and also to charactterize the transients involved through laser flash photolysis studies. The substrates that we have examined include ($\underline{E}$)-1-(2-benzylidene-1-phenylhydrazinyl)-1,2-di-benzoylethylene ($\underline{12a}$), ($\underline{E}$)-1-(2-$\underline{p}$-methylbenzylidene-1-phenylhydrazinyl)-1,2-dibenzoylethylene ($\underline{12b}$), ($\underline{E}$)-1-(2-$\underline{p}$-methoxybenzylidene-1-phenylhydrazinyl)-1,2-dibenzoylethylene ($\underline{12c}$), ($\underline{E}$)-1-(2-$\underline{p}$-cyanobenzylidene-1-phenylhydrazinyl)-1,2-dibenzoylethylene ($\underline{12d}$), ($\underline{E}$)-1-(2-$\underline{p}$-acetoxybenzylidene-1-phenylhydrazinyl)-1,2-di-benzoylethylene ($\underline{12e}$), ($\underline{E}$)-1-(2-$\underline{p}$-carbomethoxybenzylidene-1-phenylhydrazinyl)-1,2-dibenzoylethylene ($\underline{12f}$), ($\underline{E}$)-1-(2-$\underline{p}$-dimethylaminobenzylidene-1-phenylhydrazinyl)-

1,2-dibenzoylethylene (12g), and (E)-1-(2-p-chloro-
benzylidene-1-phenylhydrazinyl)-1,2-dibenzoylethylene (12h).

II.3 RESULTS AND DISCUSSION

II.3.1 Preparation of Starting Materials. It has
been reported earlier that (E)-1-(2-arylidene-1-phenyl-
hydrazinyl)-1,2-dibenzoylethylenes such as 12a,c could be
prepared in low yields by the addition of the corresponding
benzaldehyde phenylhydrazones 9a,c to dibenzoylacetylene
(DBA, 10) in refluxing methanol.[20] In the present studies
we have found that (E)-1-(2-arylidene-1-phenylhydrazinyl)-
1,2-dibenzoylethylenes 12a-h could be prepared in high
yields through the addition of the corresponding benzalde-
hyde phenylhydrazones 9a-h to DBA (10) in refluxing aceto-
nitrile and in the presence of anhydrous potassium carbo-
nate (Scheme II.2). The structures of the adducts 12a-h
have been arrived at on the basis of analytical results,
spectral data and comparison with authentic samples pre-
pared by known procedures. The stereochemistry across the
carbon-carbon double bond in 12a-h has been assigned as
that of the E configuration, on the basis of their electro-
nic spectra[20,27] and literature precedents.[28,29]

II.3.2 Preparative Photochemistry and Product Identi-
fication. Irradiation of a benzene solution of 12a for

Scheme II.2
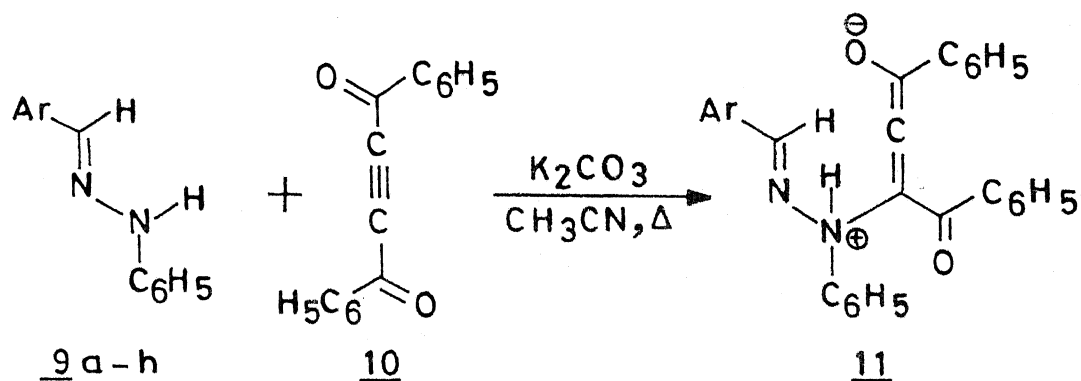
a) Ar = C$_6$H$_5$

b) Ar = C$_6$H$_4$CH$_3$-p

c) Ar = C$_6$H$_4$OCH$_3$-p

d) Ar = C$_6$H$_4$CN-p

e) Ar = C$_6$H$_4$OCOCH$_3$-p

f) Ar = C$_6$H$_4$CO$_2$CH$_3$-p

g) Ar = C$_6$H$_4$N(CH$_3$)$_2$-p

h) Ar = C$_6$H$_4$Cl-p
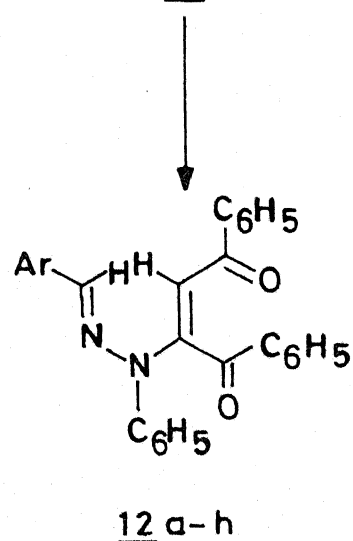
2 h gave a mixture of 4,5-dibenzoyl-1,3-diphenylpyrazole
(18a, 78%), and 1-anilino-1,2-dibenzoylethylene (19, 6%), and
a small amount (5%) of the unchanged 12a (Scheme II.3). Irra-
diation of 12a in methanol, under analogous conditions, also
gave a mixture of 18a (63%), 19 (5%), and the unchanged 12a
(28%). Similarly, the irradiation of 12b-h in benzene gave
the corresponding 3-aryl-4,5-dibenzoyl-1-phenylpyrazoles
18b (82%), 18c (68%), 18d (43%), 18e (81%), 18f (83%), 18g
(46%), and 18h (83%), respectively, along with small amounts
(1-6%) of 19, in each case. Likewise, the irradiation of
12b-h in methanol also gave 18b (66%), 18c (68%), 18d (47%),
18e (73%), 18f (77%), 18g (47%), and 18h (78%), respectively,
along with small amounts (1-6%) of 19. The results of the
irradiation experiments of 12a-h under different conditions
are summarized in Table II.1. The structures of the pyrazo-
les 18a-h were arrived at on the basis of analytical results,
spectral data and comparison with authentic samples prepared
through standard procedures.

To ascertain whether the transformations of 12a-h to
the corresponding pyrazoles occur through true photoreactions
or not, blank runs were carried out, in each case. Thus, the
stirring of benzene and methanol solutions of 12a-h, for
periods ranging from 5-15 h, around 30 $^{\circ}$C, in the dark under

Scheme II.3

a) Ar = C_6H_5

b) Ar = $C_6H_4CH_3$-p

c) Ar = $C_6H_4OCH_3$-p

d) Ar = C_6H_4CN-p

e) Ar = $C_6H_4OCOCH_3$-p

f) Ar = $C_6H_4CO_2CH_3$-p

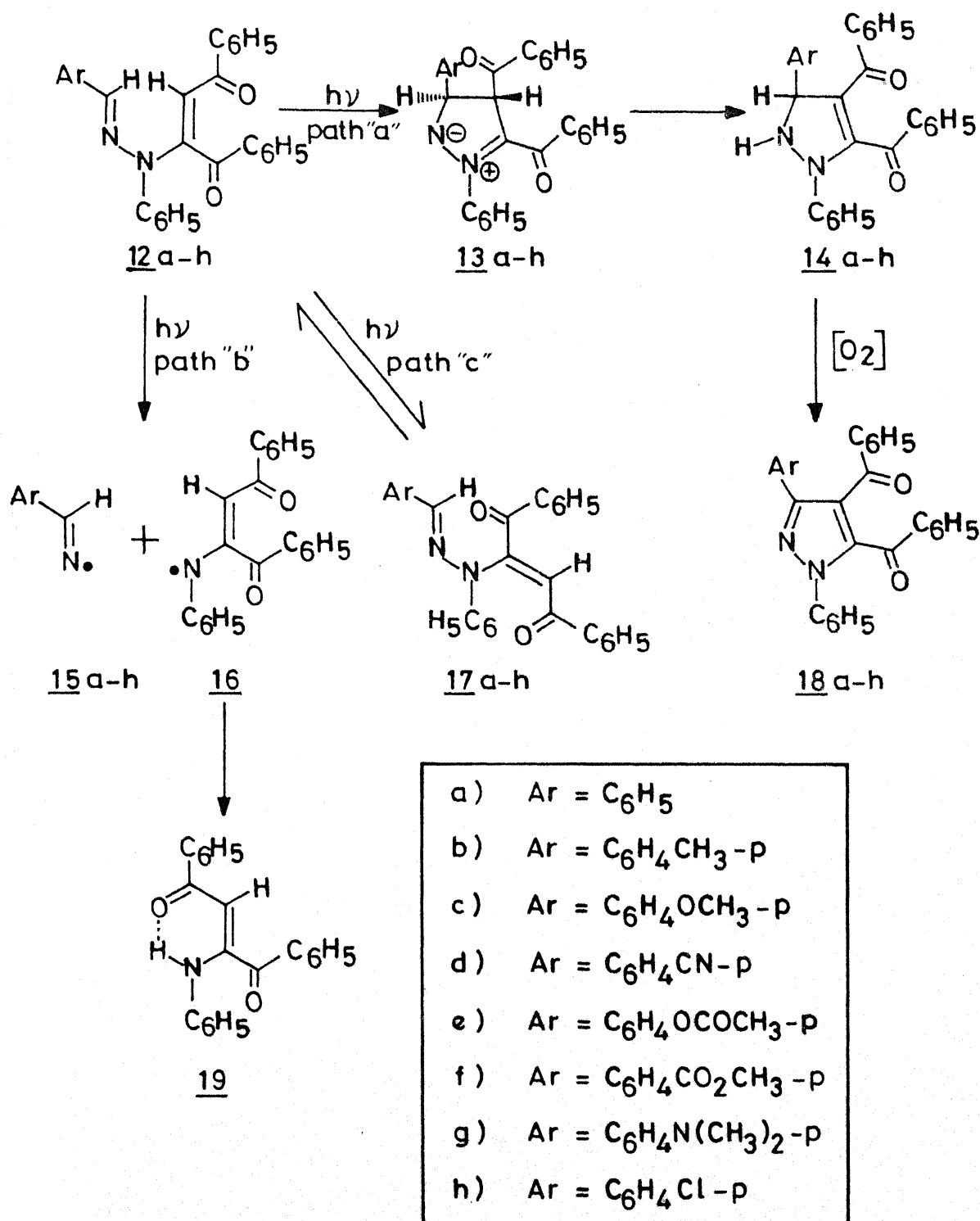g) Ar = $C_6H_4N(CH_3)_2$-p

h) Ar = C_6H_4Cl-p

Table II.1   Results of the Irradiation of (<u>E</u>)-1-(2-Arylidene-
1-phenylhydrazinyl)-1,2-dibenzoylethylenes (<u>12a-h</u>)

substrate	solvent	irradiation time, h	Product distribution, %		
			<u>18a-h</u>	<u>19</u>	unchanged <u>12a-h</u>
<u>12a</u>	benzene	2	78	6	5
	methanol	2	63	5	28
<u>12b</u>	benzene	4	82	4	–
	methanol	4	66	4	19
<u>12c</u>	benzene	5	75	6	3
	methanol	5	68	6	15
<u>12d</u>	benzene	2	43	3	22
	methanol	2	47	4	26
<u>12e</u>	benzene	2	81	1	5
	methanol	2	73	1	20
<u>12f</u>	benzene	2	83	6	–
	methanol	2	77	6	10
<u>12g</u>	benzene	12	46	6	31
	methanol	12	47	6	32
<u>12h</u>	benzene	2	81	3	6
	methanol	2	73	3	11

nitrogen atmosphere and workup in the usual manner resulted
in the recovery of unchanged 12a-h in nearly quantitative
yields, in each case. Also, in a representative run, a
benzene solution of 12a was refluxed (~80 °C) for 5 h.
Workup in the usual manner gave a nearly quantitative yield
of the unchanged 12a. However, neat heating of 12a,c in
sealed tubes at approximately 10 °C above their respective
melting points gave the corresponding pyrazoles 18a,c in
high yields (82-83%), along with small amounts (5%), of 19,
in each case.

II.3.3 <u>Laser Flash Photolysis Studies</u>.[30] In order to
gain information regarding the spin multiplicities of the
photoreactive states and the involvement of zwitterionic
intermediates such as 13a-h, in the phototransformations of
12a-h, these substrates have been subjected to laser flash
photolysis studies.

Each of the dibenzoylalkene derivatives 12a-h is chara-
cterised by a moderately strong absorption band system at
320-420 nm (λ_{max} = 370-383 nm, ε_{max} = (3.4-4.5) x 10^3 $M^{-1}cm^{-1}$
in benzene). Compared with 12a-f,h, 12g has its absorption
maximum considerably red shifted (λ_{max} = 404 nm,
ε_{max} = 4.2 x 10^3 $M^{-1}cm^{-1}$ in benzene). As a matter of fact,
both electron-donating (e.g., OCH_3 and $N(CH_3)_2$ and electron-

withdrawing (e.g., CN and CO_2CH_3) groups at the p-position
of the 2-arylidene moiety cause red shifts in λ_{max}'s suggest-
ing non-negligible electronic interaction between the enehydra-
zine and dibenzoylalkene chromophores. On going from benzene
to methanol, the absorption maxima move slightly to longer
wavelengths (shifts, 1-10 nm). Because of the strong ground
state absorptions at 337.1 and 355 nm, it was feasible to
carry out flash photolysis experiments on dilute solutions
(typically 0.1 mM) using direct laser excitation at these
wavelengths. Also, from the onsets of lowest-energy absorp-
tion band systems, the lowest singlet energies, E_S were esti-
mated to be at 70 kcal mol^{-1} or lower. Since the singlet-
triplet energy separations[31] of typical $\pi-\pi^*$ transitions are
at least 25 kcal mol^{-1}, the lowest triplet energies of 12a-h
can be reasonably located at 50 kcal mol^{-1} or lower. This
consideration is important in the selection of an appropriate
triplet sensitizer for sensitization experiments.

The major change upon laser flash photolysis (337.1 or
355 nm) of 12a-g in benzene or methanol was the bleaching of
ground state absorption at 320-450 nm. This is illustrated
in Figure II.1, with 12a as the substrate. Beyond and below
the spectral region of ground state depletion, small positive
absorbance changes due to products were observed. The moni-
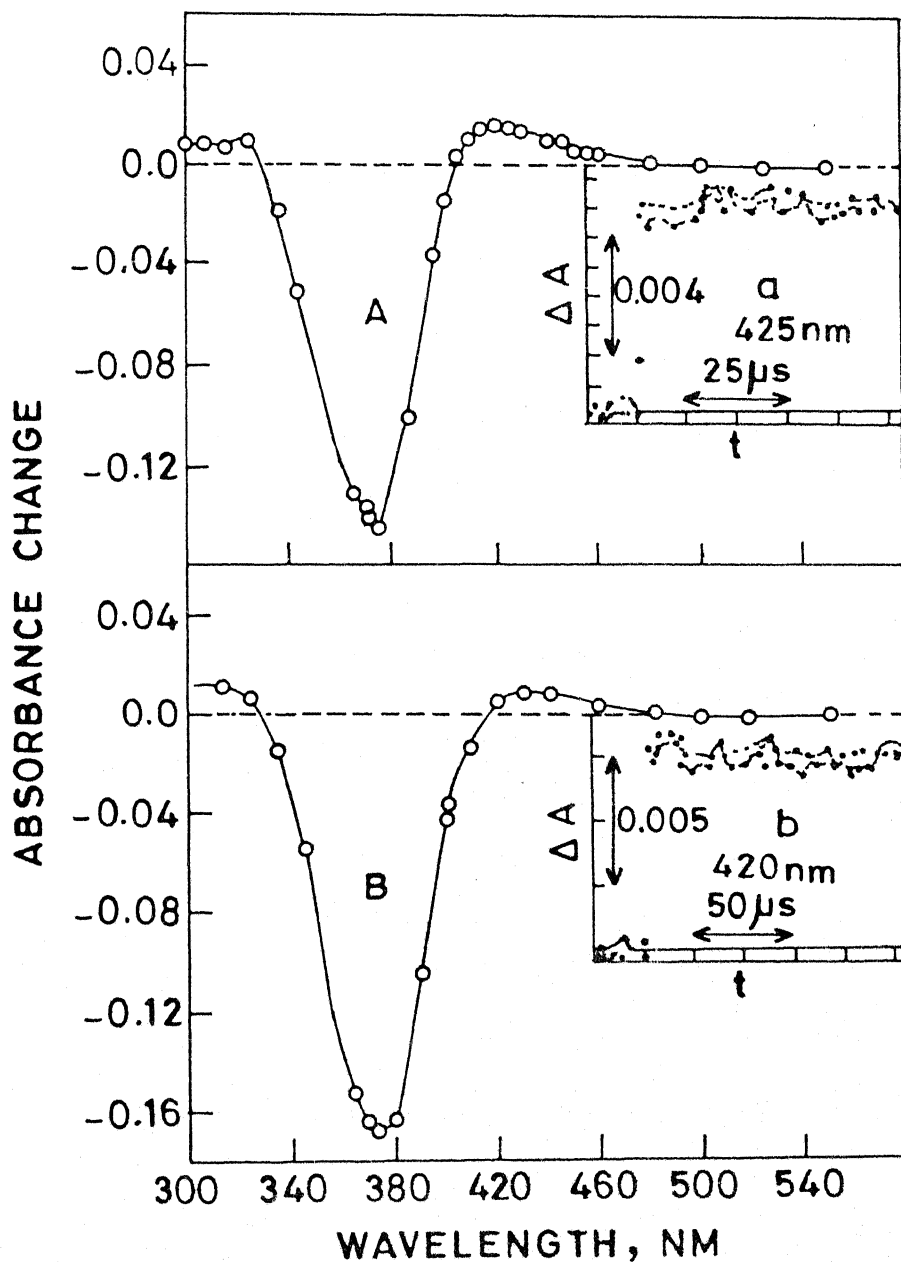toring of the photoproduct absorptions at the longest time

Figure II.1 Absorption spectral changes following 355 nm laser excitation of 12a in (A) benzene and (B) methanol. Insets: kinetic traces for transient decay in (a) benzene and (b) methanol at the wavelengths indicated.

scale (about 150 μs) showed very little ($\leq$15%) or no decay.
The presence of oxygen (about 2 mM) in the solutions did not
affect the yields or decay kinetics of the photoproducts.
Also, attempts to quench them by di-_tert_-butyl nitroxide
(DTBN) and ferrocene were unsuccessful ($k_q < 10^6$ M^{-1} s^{-1}).
Based on this, the observed transient absorbances cannot be
partially or totally due to the triplets of the dibenzoylal-
kene derivatives 12a-g.

Employing benzophenone triplet formation (in benzene)
for actinometry, the lower limits of photochemical yields
(Φ_{PC}^{lim}) were estimated from the bleaching of the ground
state absorptions. In these experiments, the end-of-pulse
absorbance change ΔA_{BP}^{T} due to benzophenone triplet at
532 nm was compared with the negative absorbance changes
ΔA_G^S at 378 nm resulting from photochemical loss of the sub-
strates under 337.1 nm or 355 nm laser excitation. The
selection of 378 nm as the wavelength for monitoring ground
state depletion was dictated by the availability of an
appropriate interference filter (Oriel 5366) with the trans-
mittance centred at this wavelength. The solutions were
optically matched (absorbance, 0.1 in 2 mm cell) at the
laser wavelength. Φ_{PC}^{lim} was calculated using the equation

$$\Phi_{PC}^{lim} = \Phi_T \left(\frac{\varepsilon_{BP}^{T}}{\varepsilon_G^{S}}\right) \left(\frac{-\Delta A_G^{S}}{\Delta A_{BP}^{T}}\right) \qquad (II.1)$$

where ε_{BP}^{T} is the extinction coefficient of benzophenone triplet (7.6×10^{3} $M^{-1}cm^{-1}$ at 532 nm in benzene),[32] Φ_T is its quantum yield (taken to be unity) and ε_{G}^{S} is the substrate ground state extinction coefficient at 378 nm. Since the extinction coefficients of the photoproducts are not necessarily negligible, the quantum yields obtained from equation II.1 represent the lower limits. The data concerning photoproduct absorption maxima and quantum yields are compiled in Table II.2. The wavelength maxima in Table II.2 correspond to _difference_ absorption spectra and do not necessarily represent the true maxima of the photoproducts.

In order to shed light on the triplets of the dibenzoylalkenes 12a-h, laser flash photolysis and pulse radiolysis experiments were carried out with camphorquinone (CQ, E_T = 52 kcal mol^{-1}),[33] biphenyl (E_T = 66 kcal mol^{-1}),[34] and 1-methylnapthalene (MN, E_T = 60 kcal mol^{-1})[34] as triplet sensitizers. Substrates 12a,c,d were used as acceptors. CQ was directly excited at the laser wavelength (485 nm) and its triplet ($^3CQ^*$) was monitored from the transient absorption at long wavelength (700 nm).[35] At the laser excitation wavelength (485 nm), the ground state absorptions were negligible at the concentrations used (0.5-2.0 mM). Figure II.2 shows representative transient absorption spectra and kinetic

Table II.2 Wavelength Maxima of Absorption Spectral Changes
and Lower Limits of Photochemical Yields in the
Course of 337.1 nm Laser Flash Photolysis of
($\underline{E}$)-1-(2-Arylidene-1-phenylhydrazinyl)-1,2-di-
benzoylethylenes ($\underline{12a-g}$)

substrate	λ_{max}^{diff}, nm		Φ_{PC}^{lim}	
	benzene	methanol	benzene	methanol
$\underline{12a}$	415	425	0.07	0.1
$\underline{12b}$	410	430	0.07	0.09
$\underline{12c}$	425	440	0.09	0.08
$\underline{12d}$	415	420	0.05	0.07
$\underline{12e}$	415	420	0.08	0.06
$\underline{12f}$	420	420	0.06	0.08
$\underline{12g}$	460	500	0.04	0.01

traces obtained with 12c as acceptor. Concomitant with the decay of $^3CQ^*$ at 700 nm, the formation of long-lived photoproduct(s) was observed at 410-500 nm. From the dependence of the pseudo-first-order rate constant for $^3CQ^*$ decay on substrate concentration, the bimolecular rate constants for the quenching of $^3CQ^*$ by 12a, 12c and 12d were estimated at $(2-3) \times 10^9$ $M^{-1}s^{-1}$ in benzene. In comparison, the observation (λ_{ex} = 485 nm) of N-methylthioacridone triplet (λ_{max}^T = 520 nm)[36] in benzene solution saturated with 12a, 12c or 12d showed that the thioketone triplet decay was affected very little by these substrates ($k_q^T < 5 \times 10^8$ $M^{-1}s^{-1}$). Since the triplet energy of N-methylthioacridone is located at 42.9 kcal mol^{-1},[37] it is concluded that the E_T of the dibenzoylalkenes under examination are bracketted by 43 and 52 kcal mol^{-1} (the latter being E_T of CQ).

In the triplet sensitization experiment using $^3CQ^*$, at all substrate concentrations (up to 4 mM), the kinetics of the growth of photoproduct absorptions at 410-500 nm matched very well with those of $^3CQ^*$ decay at 700 nm. Even at the highest substrate concentration, no relative lag was noticed in the growth of photoproducts. This strongly suggests that the triplets of 12a, 12c and 12d are too short lived (τ < 50 ns) to make their intermediacy recognized in the formation kinetics of photoproducts.
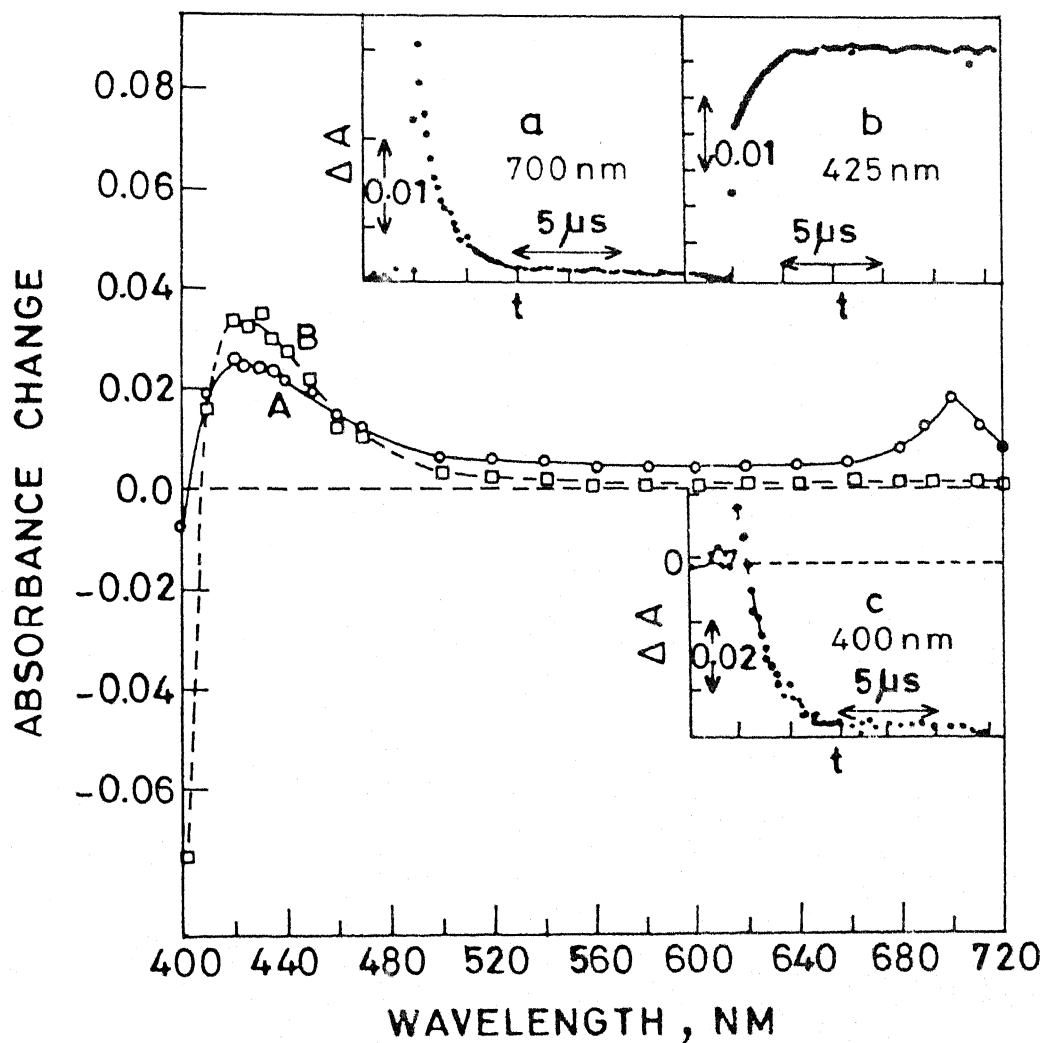
Figure II.2 Absorption changes (A) 0.05 μs and
(B) 12 μs following 485 nm laser excitation of about
0.02 M CQ in the presence of 0.5 mM 12c in benzene.
Insets: kinetic traces for transient decay at the
wavelengths indicated.

The decay of photoproducts (410-500 nm), formed under 485 nm laser excitation of CQ in benzene solution, saturated with 12a, 12c or 12d, occured very slowly over microseconds ($\tau_{1/2} > 100$ µs). The decay kinetics were complex. On a relatively short time scale (about 10 µs), in some cases, a weak first-order component ($\tau = 4$-8 µs) was noticeable at 460-480 nm. This component was slightly oxygen sensitive as shown by experiments in air-saturated solutions ($k_{q,O_2} \leq 5 \times 10^8$ $M^{-1}s^{-1}$). Unfortunately, the weak character of the short-lived transient absorption did not permit any reliable quenching studies to be carried out.

Triplet sensitization studies were also carried out using, as donors, biphenyl and MN triplets generated by pulse radiolysis[32,38] in benzene. In a typical experiment, a benzene solution of biphenyl (0.05-0.10 M) and a substrate (about 1 mM) was subjected to irradiation by an electron pulse (for about 5 ns). Biphenyl, being at a much higher concentration than the substrate, first accepts energy from the pulse-radiolytic, short-lived solvent triplet ($\tau_T = 3.4$ ns);[32] the resultant long-lived biphenyl triplet ($\tau_T > 20$ µs) then transfers energy to the substrate and triplet-mediated photoproducts from the latter are observed. The transient spectra, shown for 12a and 12c in Figure II.3,
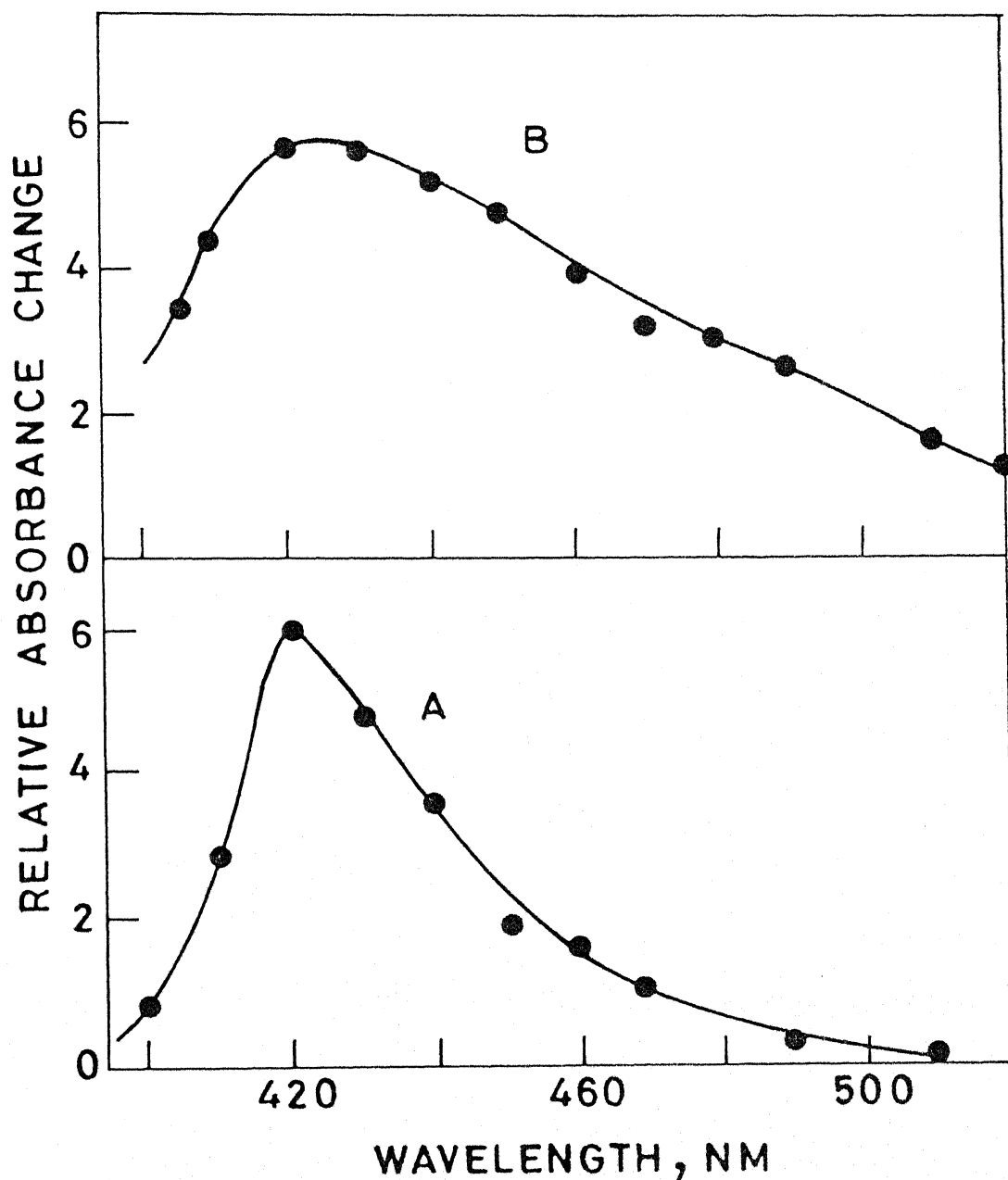
Figure II.3 Absorption changes at 5 µs following pulse radiolysis of 0.05 M biphenyl in the presence of (A) 0.5 mM 12a and (B) 0.6 mM 12c in benzene.

and the decay kinetics of the photoproducts were found to be very similar to those observed under laser flash photolysis (direct excitation as well as ^{3}CQ* sensitization, vide supra). The absorption due to biphenyl triplet at 350-400 nm was not accessible in these experiments because of its strong spectral overlap with the ground state absorptions of the substrates. However, the fact that biphenyl triplet was quenched by the substrates could be inferred from the observation that pulse-radiolytic ^{3}MN*, monitored at 425 nm was efficiently quenched by them at the same concentrations, though MN has a lower E_T (60 kcal mol^{-1}) than biphenyl (E_T = 66 kcal mol^{-1}). It was necessary to perform sensitization experiments using ^{3}CQ* and ^{3}MN* because we were apprehensive that ^{3}CQ* might be quenched by the substrates, at least in part, by electron transfer mechanism with the latter acting as electron-rich donors.

It was important to see if stable products, with absorption spectra red shifted relative to those of the reactants, were formed under photoexcitation. We carried out steady-state photolysis (366 nm) of 12a in benzene and methanol (both deaerated and air saturated) and noted the resultant absorption spectral changes. As shown in Figure II.4, while there was photochemical loss of absorbance in the region

of ground state absorption of 12a, additional absorption
indeed developed at 410-480 nm. Oxygen (about 2 mM) was
not found to have any effect on photoreaction yields. In
benzene, in the absence of oxygen, the spectrum of photolyzed
solution remained unchanged over prolonged periods (observed
over 2-4 days). However, in air-saturated benzene solution,
the red-shifted absorption due to photoproducts was slowly
lost (over days), while the absorption in the region of the
ground state spectrum (320-420 nm) was partially regained.
In methanol, deaerated or air saturated, the ground state
absorption was slowly regained at the expense of photoinduced
red-shifted absorption. All these results suggest that a
'stable' product is photogenerated from 12a, contributes to
absorptions at long wavelengths (420-480 nm) and slowly
reverts to the reactant in a protic solvent or in the presence
of oxygen. Steady-state spectral changes similar to those
under direct excitation were also noted under 485 nm irradia-
tion of CQ in the presence of 2.0 mM 12a in benzene.

The most probable species responsible for the red-
shifted absorption resulting from steady-state photolysis is
either the zwitterion 13 or the Z-isomer 17 (Scheme II.3).
It is highly unlikely that a syn-anti hydrazone isomerization
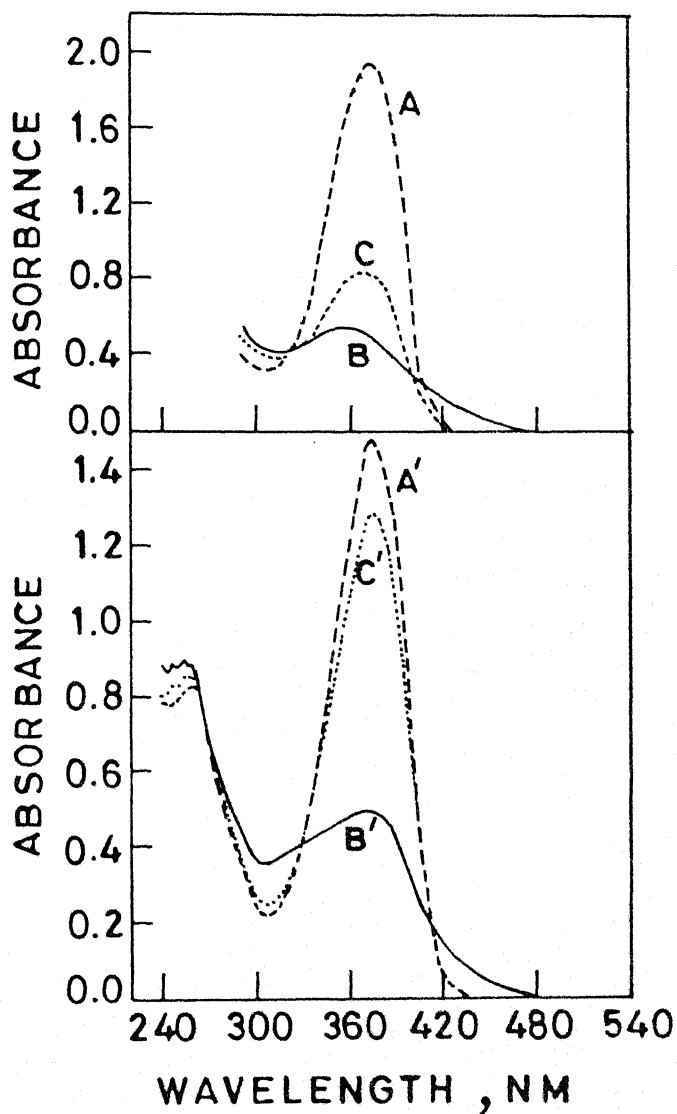would cause a large red-shift in the absorption spectrum of

Figure II.4 Absorption spectral changes as a result of steady-state irradiation of <u>12a</u> in benzene (A-C) and methanol (A'-C'). A and A', before irradiation; B and B', after 40 min. and 70 min. irradiation respectively; C, photolyzed solution (air saturated) after 48 h; C' photolysed solution (degassed) after 72 h.

the cis-dibenzoylalkene chromophore. The pyrazoline 14
and the pyrazole 18 are easily ruled out on the basis that
their absorption spectra are blue-shifted relative to the
parent substrates 12. This is actually observed for the
isolated pyrazoles (λ_{max} ~ 250 nm for 18 in methanol) and
is anticipated for pyrazolines 14 because of the loss of
interaction between the arylidene and dibenzoylalkene chro-
mophores. We prefer an assignment in terms of the Z-isomer
17 rather than the zwitterion 13, because the latter is
unlikely to be stable (over days) and there is also no
specific reason for it to revert to the reactants upon
interaction with oxygen or a protic solvent. However, the
Z-isomer would slowly isomerize to the more stable E-form
and this thermal isomerization would be catalysed by charge
transfer complexation with oxygen or protonation in a pro-
tic solvent.

That E-Z isomerization about the alkene bond occurs
in the course of the photolysis was conclusively established
by a ^{1}H NMR analysis of the photolysate from 12a in benzene-
d_6 (λ_{ex} = 366 nm). Between photolysis and NMR measurement
and during the transfer of the photolysates to the NMR
sample tubes, exposure of the solution to oxygen was care-
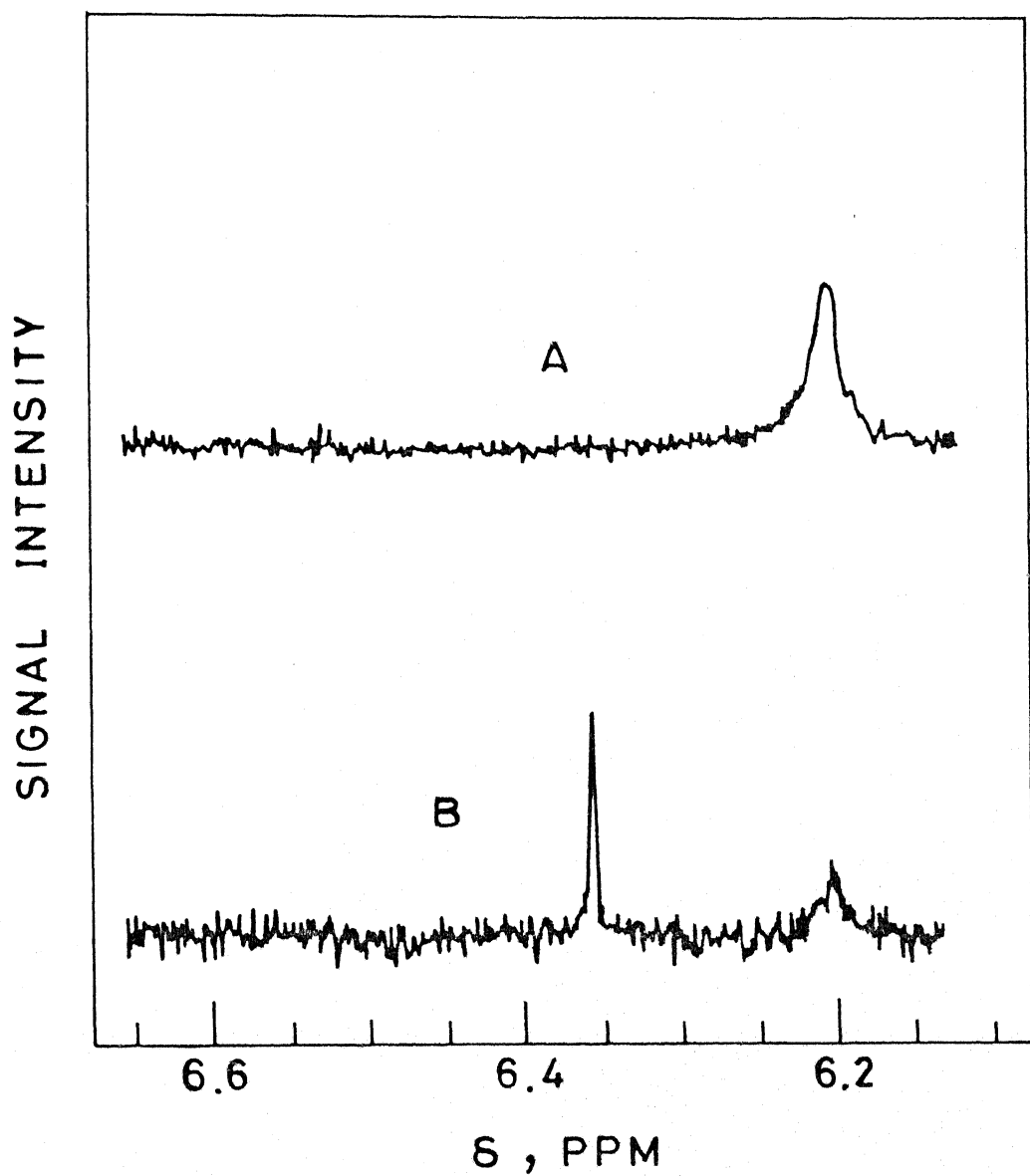fully avoided. It was found that, at the expense of the

Figure II.5 ^{1}H NMR spectra (300 MHz, vinyl region) of (A) 12a and (B) photolysate from 12a in benzene-d$_6$.

vinylic proton peak at δ 6.20 in the starting E-isomer,
a new peak developed at a slightly downfield region at
δ 6.36 after photolysis (Figure II.5). The latter is
assigned to the vinylic proton in the Z-isomer 17. The
relative vinyl proton chemical shifts in E and Z isomers
of enamine maleates/fumarates formed from the reaction
of secondary amines with dimethyl acetylenedicarboxylate[39]
are well documented in the literature.

We interpret the absorption spectral change seen upon
direct laser excitation, as well as, under triplet sensiti-
zation in terms of at least two photoproducts with closely
overlapping spectra at 410-480 nm. One is a long lived
transient with its lifetime in the microsecond to milli-
second domain. In view of the predominant photoreaction
established by preparative photochemistry and product analy-
sis, this species appears to be the zwitterion 13. The
other photoproduct is permanent and is most probably the
Z-isomer 17, as indicated by the ^{1}H NMR spectral changes
during steady-state photolysis. The triplets of 12a-h are
very short lived (less than 50 ns), but this is not surpri-
sing in the light of possible intramolecular charge transfer,
twisting about the alkene double bond and photocyclization
pathway. Our results show that the triplets are photo-
reactive. However, since they are short lived and elusive,

their intermediacy under the conditions of direct excita-
tion could not be definitively established.

II.3.4 <u>Discussion</u>. The photochemical transformation
of the dibenzoylalkenes <u>12a-h</u> to the pyrazoles <u>18a-h</u> can be
explained in terms of path 'a' shown in Scheme II.3. It is
assumed that the initial step in the reaction involves a
photochemical electrocyclic, conrotatory ring closure of the
six-electron system present in <u>12a-h</u> to give the zwitterionic
intermediates <u>13a-h</u>. Subsequent hydrogen migration through
either a [1,4] or two [1,2] shifts will lead to the pyrazol-
ines <u>14a-h</u>, which, on air-oxidation under the conditions of
workup will give rise to the pyrazoles <u>18a-h</u>, ultimately.
It may be pointed out here that numerous examples of such
photocyclizations of six electron systems, as in the cases
of diarylamines, arylvinylamines, diaryl ethers, aryl vinyl
ethers, aryl vinyl sulphides and miscellaneous divinyl
systems are reported in literature.[21-25] On the basis of
the product yields (Table II.1), both electron-donating and
electron-withdrawing groups on 2-arylidene moiety appear
compatible with such photocyclizations. However, the
electron-donating groups in <u>12b</u> (CH_3), <u>12c</u> (OCH_3), and <u>12g</u>
($N(CH_3)_2$) tend to slow down the cyclization reaction to
some extent, whereas the effect of electron-withdrawing

groups in 12e (OCOCH$_3$), 12f (CO$_2$CH$_3$) and 12h (Cl) is only
marginal, as revealed by the data presented in Table II.1.

The near quantitative recovery of 12a-h from the blank
runs carried out at 30 $^{\circ}$C, as well as of 12a, after prolonged
refluxing in benzene, as against the facile transformation
of these substrates to the pyrazoles 18a-h upon irradiation,
confirms our assumption that the cyclization reaction is
truly photochemical in nature. However, the formation of
the pyrazoles 18a,c in the high-temperature thermolysis of
12a,c indicate, that such cyclizations are feasible under
thermal conditions as well. The initial step under these
conditions may be a disrotatory cyclization of the six-
electron system in 12.

A minor pathway followed by 12a-h, under photochemical
as well as thermal conditions, lead to 1-anilino-1,2-di-
benzoylethylene (19). The formation of 19 from 12a-h may be
explained in terms of path 'b' shown in Scheme II.3, invol-
ving fragmentation across nitrogen-nitrogen bond to give the
radicals 15a-h and 16. Further reaction of 16, involving
hydrogen atom abstraction from either 15 or from the medium
will lead to 19. It may be pointed out that similar photo-
fragmentation reactions involving carbon-nitrogen bond clea-
vage have been observed in the case of several arylvinyla-
mines.[40]

It is interesting to note that none of the dibenzoylal-
kene derivatives 12a-h underwent the dibenzoylalkene rearran-
gement.[1-5] Thus, it can be concluded that the six-electron
cyclization reaction leading to the pyrazoles 18a-h is the
preferred reaction pathway for 12a-h, under the present
reaction conditions. However, that E-Z isomerization (path
'c', Scheme II.3) across the ethylenic double bond is a
major photochemical reaction pathway for 12a-h was indicated
by time-resolved studies. Our attempts to isolate the Z-
isomers 17a-h from the photolysates of 12a-h were unsuccess-
ful, presumably due to the isomerization of the Z-isomers
17a-h back to the E-isomers 12a-h, under the conditions of
workup. We have established that such isomerizations are
accelerated by oxygen and protic solvents. This, in turn,
partially accounts for the slower transformation of 12a-h
to 18a-h in methanol than in benzene (Table II.1).

II.4 EXPERIMENTAL SECTION

All melting points are uncorrected and were determined
on a Mel-Temp apparatus. The IR spectra were recorded on a
Perkin-Elmer Model 377 infrared spectrometer. The electron
spectra were recorded on Cary 17D or Cary 219 spectrometers
The ^{1}H NMR spectra were recorded on Bruker WH-90, Varian
EM-390 or Nicolet NB-300 spectrometers. The mass spectra

were recorded on a Hitachi RMU-6E single-focussing mass

spectrometer at 70 eV. Unless otherwise mentioned, all

steady-state irradiations were carried out at 20-25 °C,

employing a Hanovia 450 W medium pressure mercury lamp in a

quartz jacketed immersion well with a pyrex filter.

II.4.1 **Starting Materials**. Dibenzoylacetylene (DBA,

10),[41,42] mp 110-111 °C, benzaldehyde phenylhydrazone (**9a**),[43]

mp 158 °C, p-tolualdehyde phenylhydrazone (**9b**),[43] mp 112 °C,

p-anisaldehyde phenylhydrazone (**9c**),[43] mp 121 °C, p-cyanoben-

zaldehyde phenylhydrazone (**9d**),[44] mp 144 °C, p-acetoxybenzal-

dehyde phenylhydrazone (**9e**),[43] mp 121 °C, p-carbomethoxyben-

zaldehyde phenylhydrazone (**9f**),[44] mp 115 °C, p-dimethylamino-

benzaldehyde phenylhydrazone (**9g**),[43] mp 148 °C, and p-chloro-

benzaldehyde phenylhydrazone (**9h**),[43] mp 127 °C were prepared

by reported procedures. Solvents for steady-state photolysis

were purified and distilled before use, whereas Aldrich Gold-

Label solvents were used for laser studies. Petroleum ether

used was the fraction with bp 60-80 °C.

II.4.2 **Preparation of (E)-1-(2-Arylidene-1-phenyl-**
hydrazinyl)-1,2-dibenzoylethylenes 12a-h. A general proce-

dure for the preparation of **12a-h** was to reflux an equimolar

mixture of the phenylhydrazones **9a-h**, DBA (**10**) and anhydrous

potassium carbonate (10 mmol each) in acetonitrile (30 mL) for about 3 h. Removal of the solvent under reduced pressure gave a residual solid, which was treated with methanol and kept overnight at room temperature. The (E)-1-(2-arylidene-1-phenylhydrazinyl)-1,2-dibenzoylethylenes that separated out were purified by recrystallization from a mixture (1:2) of chloroform and methanol.

(E)-1-(2-Benzylidene-1-phenylhydrazinyl)-1,2-dibenzoylethylene (12a).[20] 12a was obtained in a 63% yield, mp 206-207 °C (mixture melting point).

(E)-1-(2-p-Methylbenzylidene-1-phenylhydrazinyl)-1,2-dibenzoylethylene (12b). 12b was obtained in a 66% yield, mp 185-186 °C.

IR spectrum ν_{max} (KBr): 3050, 2910 (CH), 1680 (C=O), 1625, 1590 and 1520 (C=N and C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 254 nm (ε, 25,200) and 378 (41,000).

^{1}H NMR spectrum (CDCl$_3$): δ 2.27 (3 H, s, methyl), 5.96 (1 H, s, vinylic), and 7.51 (20 H, m, aromatic and benzylidenic).

Mass spectrum m/e (relative intensity): 444 (M$^+$, 26),

442 (M^+ - 2 H, 37), 365 (M^+ - 2 H, - C_6H_5, 15), 339 (M^+ - C_6H_5CO, 65), 105 ($C_6H_5CO^+$, 100), and other peaks.

Anal. Calcd for $C_{30}H_{24}N_2O_2$: C, 81.08; H, 5.41; N, 6.31. Found: C, 81.32; H, 5.40; N, 6.25.

(E)-1-(2-p-Methoxybenzylidene-1-phenylhydrazinyl)-1,2-dibenzoylethylene (12c).[20] 12c was obtained in a 68% yield, mp 209 °C (mixture melting point).

(E)-1-(2-p-Cyanobenzylidene-1-phenylhydrazinyl)-1,2-dibenzoylethylene (12d). 12d was obtained in a 70% yield, mp 231-232 °C.

IR spectrum ν_{max} (KBr): 3060 (CH), 2215 (C≡N), 1685 (C=O), 1620, 1590 and 1520 (C=N) and (C=C) cm^{-1}.

UV spectrum λ_{max} (CH_3OH): 259 nm (ε, 26,700) and 384 (49,000).

^{1}H NMR spectrum ($CDCl_3$): δ 6.00 (1 H, s, vinylic) and 7.61 (20 H, m, aromatic and benzylidenic).

Anal. Calcd for $C_{30}H_{21}N_3O_2$: C, 79.12; H, 4.62; N, 9.23. Found: C, 78.73; H, 4.60; N, 9.51.

(E)-1-(2-p-Acetoxybenzylidene-1-phenylhydrazinyl)-1,2-dibenzoylethylene (12e). 12e was isolated in a 61% yield, mp 201-202 °C.

IR spectrum ν_{max} (KBr): 3060, 3010 (CH), 1760, 1685 (C=O), 1620, 1590, 1565 and 1520 (C=N and C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 252 nm (ε, 42,400), 374 (42,000).

^{1}H NMR spectrum (CDCl$_3$): δ 2.22 (3 H, s, acetoxy), 6.00 (1 H, s, vinylic), and 7.49 (20 H, m, aromatic and benzylidenic).

<u>Anal</u>. Calcd for C$_{31}$H$_{24}$N$_2$O$_4$: C, 76.03; H, 4.92; N, 5.74. Found: C, 76.41; H, 5.05; N, 5.70.

(<u>E</u>)-1-(2-<u>p</u>-Carbomethoxybenzylidene-1-phenylhydrazinyl)-1,2-dibenzoylethylene (<u>12f</u>). <u>12f</u> was obtained in a 61% yield, mp 180-181 °C.

IR spectrum ν_{max} (KBr): 3060, 2950 (CH), 1725, 1685 (C=O), 1630, 1595 and 1550 (C=N and C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 246 nm (ε, 30,100) and 384 (45,000).

^{1}H NMR spectrum (CDCl$_3$): δ 3.84 (3 H, s, carbomethoxy), 5.96 (1 H, s, vinylic), and 7.67 (20 H, m, aromatic and benzylidenic).

<u>Anal</u>. Calcd for C$_{31}$H$_{24}$N$_2$O$_4$: C, 76.03; H, 4.92; N, 5.74. Found: C, 76.25; H, 4.98; N, 5.78.

(E)-1-(2-p-Dimethylaminobenzylidene-1-phenylhydrazinyl)-1,2-dibenzoylethylene (12g). 12g was isolated in a 68% yield, mp 233-234 °C.

IR spectrum ν_{max} (KBr): 3050, 2980 (CH), 1680 (C=O), 1610, 1590 and 1560 (C=N and C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 253 nm (ε, 27,400) and 414 (43,000).

^{1}H NMR spectrum (CDCl$_3$): δ 2.89 (6 H, s, N(CH$_3$)$_2$), 6.00 (1 H, s, vinylic), and 7.37 (20 H, m, aromatic and benzylidenic).

Mass spectrum, m/e (relative intensity): 473 (M$^+$, 20), 471 (M$^+$ - 2 H, 100), 368 (M$^+$ - C$_6$H$_5$CO, 15), 366 (M$^+$ - 2 H, - C$_6$H$_5$CO, 15), and other peaks.

Anal. Calcd for C$_{31}$H$_{27}$N$_3$O$_2$: C, 78.65; H, 5.71; N, 8.88. Found: C, 79.05; H, 5.70; N, 8.82.

(E)-1-(2-p-Chlorobenzylidene-1-phenylhydrazinyl)-1,2-dibenzoylethylene (12h). 12h was obtained in a 63% yield, mp 211-212 °C.

IR spectrum ν_{max} (KBr): 3060, 3030 (CH), 1680 (C=O), 1620 and 1590 (C=N and C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 255 nm (ε, 23,700) and 375 (42,500).

^{1}H NMR spectrum (CDCl$_3$): δ 6.05 (1 H, s, vinylic) and 7.65 (20 H, m, aromatic and benzylidenic).

__Anal__. Calcd for C$_{29}$H$_{21}$N$_2$O$_2$Cl: C, 75.00; H, 4.53; N, 6.03. Found: C, 75.12; H, 4.42; N, 6.11.

II.4.3 __Irradiation of (E)-1-(2-Benzylidene-1-phenyl-hydrazinyl)-1,2-dibenzoylethylene (12a)__.[20] A solution of __12a__ (430 mg, 1 mmol) in benzene (175 mL) was irradiated for 2 h. The photolysate, after removal of the solvent under reduced pressure, was chromatographed over silica gel. Elution with a mixture (1:4) of benzene and petroleum gave 20 mg (6%) of __19__,[45] mp 130 °C (mixture melting point), after recrystallization from methanol. Subsequent elution with a mixture (3:2) of benzene and petroleum ether gave 350 mg (78%) of 4,5-dibenzoyl-1,3-diphenylpyrazole (__18a__), mp 136 °C (mixture melting point) after recrystallization from a mixture (1:1) of benzene and petroleum ether. Further elution with benzene yielded 22 mg (5%) of the unchanged __12a__, mp 206-207 °C (mixture melting point).

In a repeat run, irradiation and workup of a methanol solution of __12a__ (430 mg, 1 mmol in 175 mL) under identical conditions gave 15 mg (5%) of __19__, mp 130 °C (mixture melting point), 270 mg (63%) of __18a__, mp 136 °C (mixture melting point) and the unchanged __12a__, mp 206-207 °C (mixture melting point).

II.4.4 Irradiation of (E)-1-(2-p-Methylbenzylidene-
1-phenylhydrazinyl)-1,2-dibenzoylethylene (12b). A benzene
solution of 12b (890 mg, 2 mmol in 175 mL) was irradiated
for 4 h. Solvent was removed under reduced pressure and the
residue was chromatographed over silica gel. Elution with a
mixture (1:4) of benzene and petroleum ether gave 30 mg (4%)
of 19, mp 130 °C (mixture melting point). Further elution
with a mixture (3:2) of benzene and petroleum ether gave
735 mg (82%) of 18b, mp 130-131 °C, after recrystallization
from a mixture (1:1) of benzene and petroleum ether.

IR spectrum ν_{max} (KBr): 3060, 3000, 2910 (CH), 1660,
1640 (C=O), 1590 and 1580 (C=N and C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 253 nm (ε, 53,300).

^{1}H NMR spectrum (CDCl$_3$): δ 2.27 (3 H, s, methyl) and
7.31 (19 H, m, aromatic).

Anal. Calcd for C$_{30}$H$_{22}$N$_2$O$_2$: C, 81.45; H, 4.98; N, 6.33.
Found: C, 81.80; H, 4.53; N, 6.35.

In a repeat run, a solution of 12b (445 mg, 1 mmol) in
methanol (175 mL) was irradiated and worked up under analo-
gous conditions to give 13 mg (4%) of 19, mp 130 °C (mixture
melting point), 290 mg (66%) of 18b, mp 130-131 °C (mixture
melting point) and 85 mg (19%) of the unchanged 12b, mp 185-
186 °C (mixture melting point).

II.4.5 Irradiation of (E)-1-(2-p-Methoxybenzylidene-
1-phenylhydrazinyl)-1,2-dibenzoylethylene (12c).[20] A solu-
tion of 12c (920 mg, 2 mmol) in benzene (175 mL) was irradia-
ted for 5 h. Solvent was removed under reduced pressure and
the residue was chromatographed over silica gel. Elution
with a mixture (1:4) of benzene and petroleum ether gave
40 mg (6%) of 19, mp 130 °C (mixture melting point). Subse-
quent elution with a mixture (3:2) of benzene and petroleum
ether gave 675 mg (75%) of 18c, mp 133 °C (mixture melting
point), after recrystallization from a mixture (1:1) of ben-
zene and petroleum ether. Elution was continued with benzene
to separate 28 mg (3%) of the unchanged 12c, mp 209 °C (mix-
ture melting point).

In a repeat run, a methanol solution of 12c (460 mg,
1 mmol in 175 mL) was irradiated for 5 h and worked up as in
the earlier case to give 20 mg (6%) of 19, mp 130 °C (mixture
melting point), 315 mg (68%) of 18c, mp 133 °C (mixture
melting point) and 70 mg (15%) of the unchanged 12c, mp 209 °C
(mixture melting point).

II.4.6 Irradiation of (E)-1-(2-p-Cyanobenzylidene-
1-phenylhydrazinyl)-1,2-dibenzoylethylene (12d). A solution
of 12d (910 mg, 2 mmol) in benzene (175 mL) was irradiated

for 2 h. The photolysate, after removal of the solvent under reduced pressure, was chromatographed over silica gel. Elution with a mixture (1:4) of benzene and petroleum ether gave 20 mg (3%) of 19, mp 130 °C (mixture melting point). Further elution with a mixture (4:1) of benzene and petroleum ether yielded 380 mg (43%) of 18d, mp 145-146 °C, after recrystallization from a mixture (1:1) of benzene and petroleum ether.

IR spectrum ν_{max} (KBr): 3060, 3030 (CH), 2230 (C≡N), 1660, 1650 (C=O), 1610, 1590 and 1580 (C=N and C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 251 nm (ε, 45,000).

^{1}H NMR spectrum (CDCl$_3$): δ 7.48 (m, aromatic).

Anal. Calcd for C$_{30}$H$_{19}$N$_3$O$_2$: C, 79.47; H, 4.19; N, 9.27. Found: C, 79.12; H, 4.55; N, 9.41.

Subsequent elution with benzene gave 200 mg (22%) of the unchanged 12d, mp 231-232 °C (mixture melting point).

In a repeat run, irradiation of a methanol solution of 12d (455 mg, 1 mmol in 175 mL), followed by workup as in the earlier case, gave a mixture consisting of 13 mg (4%) of 19, mp 130 °C (mixture melting point), 210 mg (47%) of 18d, mp 145-146 °C (mixture melting point) and 118 mg (26%) of the unchanged 12d, mp 231-232 °C (mixture melting point).

II.4.7 Irradiation of (E)-1-(2-p-Acetoxybenzylidene-1-phenylhydrazinyl)-1,2-dibenzoylethylene (12e). A solution of 12e (980 mg, 2 mmol) in benzene (175 mL) was irradiated for 2 h. Solvent was removed under reduced pressure and the residue was chromatographed over silica gel. Elution with a mixture (1:4) of benzene and petroleum ether gave 5 mg (1%) of 19, mp 130 °C (mixture melting point). Further elution with a mixture (3:2) of benzene and petroleum ether gave 760 mg (81%) of 18e, mp 153-154 °C, after recrystallization from a mixture (1:1) of benzene and petroleum ether.

IR spectrum ν_{max} (KBr): 3060 (CH), 1760, 1650 (C=O), 1590 and 1575 (C=N and C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 252 nm (ϵ, 40,100).

^{1}H NMR spectrum (CDCl$_3$): δ 2.30 (3 H, s, acetoxy) and 7.28 (19 H, m, aromatic).

Mass spectrum m/e (relative intensity): 486 (M$^+$, 92), 443 (M$^+$ - CH$_3$CO, 100), 338 (M$^+$ - CH$_3$CO, - C$_6$H$_5$CO, 10) and other peaks.

Anal. Calcd for C$_{31}$H$_{22}$N$_2$O$_4$: C, 76.54; H, 4.53; N, 5.76. Found: C, 76.50; H, 4.53; N, 5.73.

Subsequent elution with benzene gave 50 mg (5%) of the unchanged 12e, mp 201-202 °C (mixture melting point).

In a repeat run, the irradiation of 12e (490 mg, 1 mmol) in methanol (175 mL) was carried out for 2 h, followed by workup under analogous conditions, to give 5 mg (1%) of 19, mp 130 °C (mixture melting point), 370 mg (73%) of 18e, mp 153-154 °C (mixture melting point) and 98 mg (20%) of the unchanged 12e, mp 201-202 °C (mixture melting point).

II.4.8   Irradiation of (E)-1-(2-p-Carbomethoxybenzylidene-1-phenylhydrazinyl)-1,2-dibenzoylethylene (12f).   A benzene solution of 12f (490 mg, 1 mmol in 175 mL) was irradiated for 2 h and the photolysate, after removal of the solvent under reduced pressure, was chromatographed over silica gel. Elution with a mixture (1:4) of benzene and petroleum ether gave 20 mg (6%) of 19, mp 130 °C (mixture melting point). Further elution with a mixture (3:2) of benzene and petroleum ether gave 410 mg (83%) of 18f, mp 200-201 °C, after recrystallization from a mixture (1:1) of benzene and petroleum ether.

IR spectrum ν_{max} (KBr): 3050, 3000, 2930 (CH), 1715, 1650 (C=O), 1610, 1590 and 1580 (C=N and C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 254 nm (ε, 30,800).

^{1}H NMR spectrum (CDCl$_3$): δ 3.90 (3 H, s, carbomethoxy) and 7.50 (19 H, m, aromatic).

Anal. Calcd for $C_{31}H_{22}N_2O_4$: C, 76.54; H, 4.53; N, 5.76. Found: C, 76.55; H, 4.68; N, 5.81.

In a repeat experiment, irradiation and workup of a methanol solution of 12f (490 mg, 1 mmol in 175 mL) under analogous conditions, gave a mixture of 19 (20 mg, 6%), mp 130 °C (mixture melting point), 18f (370 mg, 77%), mp 200-201 °C (mixture melting point) and the unchanged 12f (50 mg, 10%, elution with benzene), mp 180-181 °C (mixture melting point).

II.4.9 Irradiation of (E)-1-(2-p-Dimethylaminobenzylidene-1-phenylhydrazinyl)-1,2-dibenzoylethylene (12g). A solution of 12g (475 mg, 1 mmol) in benzene (175 mL) was irradiated for 12 h. Solvent was removed under reduced pressure and the residue was chromatographed over silica gel. Elution with a mixture (1:4) of benzene and petroleum ether gave 20 mg (6%) of 19, mp 130 °C (mixture melting point). Further elution with a mixture (4:1) of benzene and petroleum ether gave 215 mg (46%) of 18g, mp 155-156 °C, after recrystallization from a mixture (1:1) of benzene and petroleum ether.

IR spectrum ν_{max} (KBr): 3060, 2900 (CH), 1660, 1640 (C=O), 1610, 1590 and 1575 (C=N and C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 258 nm (ε, 33,700).

^{1}H NMR spectrum (CDCl$_3$): δ 2.95 (6 H, s, N(CH$_3$)$_2$) and 7.15 (19 H, m, aromatic).

<u>Anal</u>. Calcd for C$_{31}$H$_{25}$N$_3$O$_2$: C, 78.98; H, 5.31; N, 8.92. Found: C, 79.10; H, 5.25; N, 9.15.

Subsequent elution with a mixture (9:1) of benzene and ethyl acetate gave 145 mg (31%) of the unchanged <u>12g</u>, mp 233-234 $^{\circ}$C (mixture melting point).

In a repeat run, irradiation and workup of a methanol solution of <u>12g</u> (475 mg, 1 mmol in 175 mL), under analogous conditions, gave a mixture of <u>19</u> (20 mg, 6%), mp 130 $^{\circ}$C (mixture melting point), <u>18g</u> (220 mg, 47%), mp 155-156 $^{\circ}$C (mixture melting point) and the unchanged <u>12g</u> (150 mg, 32%), mp 233-234 $^{\circ}$C (mixture melting point).

II.4.10 <u>Irradiation of (<u>E</u>)-1-(2-<u>p</u>-Chlorobenzylidene-1-phenylhydrazinyl)-1,2-dibenzoylethylene</u> (<u>12h</u>). A solution of <u>12h</u> (465 mg, 1 mmol) in benzene (175 mL) was irradiated for 2 h. Solvent was removed under reduced pressure and the product mixture was chromatographed over silica gel. Elution with a mixture (1:4) of benzene and petroleum ether gave 10 mg (3%) of <u>19</u>, mp 130 $^{\circ}$C (mixture melting point). Further elution with a mixture (3:2) of benzene and petroleum

ether gave 375 mg (81%) of 18h, mp 128-129 °C, after recrystallization from a mixture (1:1) of benzene and petroleum ether.

IR spectrum ν_{max} (KBr): 3050 (CH), 1660, 1640 (C=O), 1590 and 1580 (C=N and C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 255 nm (ε, 45,500).

^{1}H NMR spectrum (CDCl$_3$): δ 7.40 (m, aromatic).

Anal. Calcd for C$_{29}$H$_{19}$N$_2$O$_2$Cl: C, 75.32; H, 4.11; N, 6.06. Found: C, 75.11; H, 4.40; N, 6.21.

Subsequent elution with benzene gave 28 mg (6%) of the unchanged 12h, mp 211-212 °C (mixture melting point).

In a repeat run, irradiation and workup of a methanol solution of 12h, under analogous conditions, gave 10 mg (3%) of 19, mp 130 °C (mixture melting point), 340 mg (73%) of 18h, mp 128-129 °C (mixture melting point) and 50 mg (11%) of the unchanged 12h, mp 211-212 °C (mixture melting point).

II.4.11 Attempted Thermal Transformation of (E)-1-(2-Arylidene-1-phenylhydrazinyl)-1,2-dibenzoylethylenes 12a-h in Benzene and Methanol (Blank Runs). Blank runs were carried out by stirring solutions of 12a-h in benzene and methanol (4 mmolar) around 30 °C in the dark for 5-15 h. Workup in

the usual manner gave back unchanged 12a-h, in each case, in nearly quantitative amounts.

II.4.12 Attempted Thermal Transformation of (E)-1-(2-Benzylidene-1-phenylhydrazinyl)-1,2-dibenzoylethylene (12a) in Refluxing Benzene. A solution of 12a (430 mg, 1 mmol) in benzene (175 mL) was refluxed in the dark for 5 h. The solution was cooled and passed through a column of silica gel to recover 410 mg (95%) of the unchanged 12a, mp 206-207 $^{\circ}$C (mixture melting point).

II.4.13 Thermal Transformation of (E)-1-(2-Benzylidene-1-phenylhydrazinyl)-1,2-dibenzoylethylene (12a)(Neat Heating at 215 $^{\circ}$C). A sample of 12a (860 mg, 2 mmol) was heated around 215 $^{\circ}$C in a sealed tube for 1 h. The product mixture was chromatographed over silica gel. Elution with a mixture (1:4) of benzene and petroleum ether gave 35 mg (5%) of 19, mp 130 $^{\circ}$C (mixture melting point). Further elution with a mixture (3:2) of benzene and petroleum ether gave 695 mg (82%) of 18a, mp 136 $^{\circ}$C (mixture melting point).

II.4.14 Thermal Transformation of (E)-1-(2-p-Methoxybenzylidene-1-phenylhydrazinyl)-1,2-dibenzoylethylene (12c) (Neat Heating at 215 $^{\circ}$C). A sample of 12c (460 mg, 1 mmol) was heated around 215 $^{\circ}$C in a sealed tube for 1 h. The

product mixture was chromatographed over silica gel. Elution with a mixture (1:4) of benzene and petroleum ether gave 15 mg (5%) of 19, mp 130 °C (mixture melting point). Further elution with a mixture (3:2) of benzene and petroleum ether gave 282 mg (83%) of 18c, mp 133 °C (mixture melting point).

II.4.15 <u>Laser Flash Photolysis</u>.[30] For most of the laser flash photolysis experiments, use was made of pulse excitation at 337.1 nm (2-3 mJ, about 8 ns, Molectron UV-400 nitrogen laser source) in a computer-controlled set-up. Laser pulses at 355 nm (10 mJ or less, about 6 ns) and 485 nm (4-6 mJ, about 6 ns) obtained from Quanta-Ray DCR-1 Nd-YAG and PDL-1 dye laser sources were also used in some of the experiments. The system is fully interfaced with an LSI 11 microprocessor which controls the experiment, average signals and processes the data. The storage and further processing of data were performed in a time-shared PDP 11/55 system. Details of the kinetic spectrophotometer, signal processing and experimental procedures are given elsewhere.[46-48]

II.4.16 <u>Pulse Radiolysis</u>.[30] For pulse radiolysis, use has been made of a computer-controlled apparatus, which allows

determination of transient absorption spectra at various times (nanosecond to second) after the electron pulse and kinetic measurements of the spectral changes. The pulse electron source was the Notre Dame 7 MeV ARCO LP-7 linear accelerator. A description of the set-up is available elsewhere.[49-50]

II.4.17 Steady-state Irradiation for Absorption Spectral Changes.[30] The irradiation was carried out in 1 cm x 1 cm quartz cells with optically flat surfaces. For 366 nm excitation, a set-up consisting of a medium pressure mercury lamp (Bausch and Lomb SP-200) and a monochromator (Bausch and Lomb 33-86-07) was used. The source of 485 nm excitation was a xenon lamp (Eimac 450 W) coupled with a monochromator (Bausch and Lomb 33-86-07). The absorption spectra were recorded on a Cary 219 spectrometer (1 nm bandpass).

II.4.18 Steady-state Irradiation for ^{1}H NMR Spectral Changes.[30] The irradiation was carried out at 366 nm (Bausch and Lomb SP-200 mercury lamp coupled with a Bausch and Lomb 33-86-07 monochromator) for 3/4 h on 1 mL of about 5 mM solution of 12a in benzene-d_6, in a quartz cell of pathlength 2 mm, under argon atmosphere. The ^{1}H NMR traces were recorded on a Nicolet NB-300 NMR spectrometer.

II.5 REFERENCES

(1)   G. W. Griffin and E. J. O'Connel, J. Am. Chem. Soc., 84, 4148 (1962).

(2)   H. E. Zimmerman, H. G. C. Dürr, R. G. Lewis and S. Braun, J. Am. Chem. Soc., 84, 4149 (1962).

(3)   A. Padwa, D. Crumrine and A. Schubber, J. Am. Chem. Soc., 88, 3064 (1966).

(4)   H. E. Zimmerman, H. G. C. Dürr, R. S. Givens and R. G. Lewis, J. Am. Chem. Soc., 89, 1863 (1967).

(5)   N. Sugiyama and C. Kashima, Bull. Chem. Soc. Jpn., 43, 1875 (1970).

(6)   S. Lahiri, V. Dabral, S. M. S. Chauhan, E. Chackachery, C. V. Kumar, J. C. Scaiano and M. V. George, J. Org. Chem., 45, 3782 (1980).

(7)   H. V. Halben, H. Schmidt and M. Hochweber, Helv. Chim. Acta, 30, 1135 (1947).

(8)   B. A. R. C. Murty, S. Pratapan, C. V. Kumar, P. K. Das and M. V. George, J. Org. Chem., 50, 2533 (1985).

(9)   B. A. R. C. Murty, C. V. Kumar, V. Dabral, P. K. Das and M. V. George, J. Org. Chem., 49, 4165 (1984).

(10) B. A. R. C. Murty, Ph. D. Thesis, Indian Institute of Technology, Kanpur, India (1982).

(11) C. V. Kumar, B. A. R. C. Murty, S. Lahiri, E. Chackachery, J. C. Scaiano and M. V. George, J. Org. Chem., 49, 4923 (1984).

(12) C. V. Kumar, Ph. D. Thesis, Indian Institute of Technology, Kanpur, India (1981).

(13) B. B. Lohray, C. V. Kumar, P. K. Das and M. V. George, J. Org. Chem., 49, 4647 (1984).

(14) B. B. Lohray, Ph. D. Thesis, Indian Institute of Technology, Kanpur, India (1982).

(15) R. Barik, K. Bhattacharyya, P. K. Das and M. V. George, J. Org. Chem., 51, 3420 (1986).

(16) R. Barik, Ph. D. Thesis, Indian Institute of Technology, Kanpur, India (1986).

(17) R. Barik, C. V. Kumar, P. K. Das and M. V. George, J. Org. Chem., 50, 4309 (1985).

(18) D. Ramaiah, S. Rajadurai, P. K. Das and M. V. George, J. Org. Chem., 52, 1082 (1987).

(19) For some pertinent references on the photochemistry of barrelenes, see Chapter I of this thesis.

(20) P. M. Scaria, Ph. D. Thesis, Indian Institute of Technology, Kanpur, India (1981).

(21) R. Huisgen, Angew. Chem. Int. Ed. Engl., 19, 947 (1980).

(22) E. C. Taylor and I. J. Turchi, Chem. Rev., 79, 181 (1979).

(23) A. A. Leone and P. S. Mariano, Rev. Chem. Intermed., 4, 81 (1981).

(24) A. G. Schultz, Acc. Chem. Res., 16, 210 (1983).

(25) A. G. Schultz and L. Motyaka, "Organic Photochemistry", A. Padwa, Ed., Marcel Dekker, New York, Vol. 6, P. 1 (1983).

(26) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Verlag Chemie, Weinheim (1970).

(27) S. Lahiri, M. P. Mahajan, R. Prasad and M. V. George, Tetrahedron, 33, 3159 (1977).

(28) W. Sucrow and M. Slopainka, Chem. Ber., 105, 3807 (1972).

(29) V. Bardakos, W. Sucrow and A. Fehlaner, Chem. Ber., 108, 2161 (1975).

(30) All laser flash photolysis and pulse radiolysis studies and steady-state irradiation for absorption spectral and ^{1}H NMR spectral changes were carried out by Dr. P. K. Das, Dr. K. Bhattacharyya and Professor M. V. George at the Radiation Laboratory, University of Notre Dame, U. S. A.

(31) S. P. McGlynn, T. Azumi and M. Kinoshita, "The Triplet State", Prentice-Hall, Englewood Cliffs, NJ, Chapter 3 (1969).

(32) R. Bensasson and E. J. Land, Photochem. Photobiol. Rev., 3, 163 (1978).

(33) T. R. Evans and P. A. Leermakers, J. Am. Chem. Soc., 89, 4380 (1967).

(34) S. L. Murov, "Handbook of Photochemistry", Marcel Dekker, New York (1973).

(35) A. Singh, A. R. Scott and F. Sopehyshyn, J. Phys. Chem., 73, 2633 (1969).

(36) C. V. Kumar, H. F. Davis and P. K. Das, Chem. Phys. Lett., 109, 184 (1984).

(37) A. Safarzadeh-Amiri, R. E. Verrall and R. P. Steer, Can. J. Chem., 61, 894 (1983).

(38) J. K. Thomas, Ann. Rev. Phys. Chem., 21, 17 (1970).

(39) K. Berbig, R. Huisgen and H. Huber, Chem. Ber., 99, 2546 (1966).

(40) M. Riviere, N. Paillous and M. A. Lattes, Bull. Soc. Chim. Fr., 1911 (1974).

(41) R. E. Lutz and W. R. Smithey, J. Org. Chem., 16, 51 (1951).

(42) R. E. Lutz, "Organic Syntheses", E. C. Horning, Ed., Wiley, New York, Coll. Vol. 3, P. 248 (1955).

(43) A. I. Vogel, "A Text Book of Practical Organic Chemistry", English Language Book Society and Longman Group Ltd., London, p. 135 (1973).

(44) H. B. Hass and M. L. Bender, J. Am. Chem. Soc., 71, 1767 (1949).

(45) S. Lahiri, Ph. D. Thesis, Indian Institute of
      Technology, Kanpur, India (1977).

(46) R. D. Small, Jr. and J. C. Scaiano, J. Am. Chem.
      Soc., 101, 6965 (1979).

(47) P. K. Das and K. Bobrowski, J. Chem. Soc., Faraday
      Trans. II, 77, 1009 (1981).

(48) V. Nagarajan and R. W. Fessenden, J. Phys. Chem., 89,
      2330 (1985).

(49) L. K. Patterson and J. Lilie, Int. J. Radiat. Phys.
      Chem., 61, 129 (1974).

(50) R. S. Schuler, Chem. Ed., 2, 34 (1987).

CHAPTER III

PHOTOCHEMICAL TRANSFORMATIONS OF A FEW 5-ARYL-3,3-DI-
PHENYL-2(3H)-FURANONES

III.1 ABSTRACT

The photochemical transformations of a few 5-aryl-
3,3-diphenyl-2(3H)-furanones such as 3,3-diphenyl-5-(4-me-
thylphenyl)-2(3H)-furanone (5b), 3,3-diphenyl-5-(4-ethyl-
phenyl)-2(3H)-furanone (5c), 3,3-diphenyl-5-(4-methoxy-
phenyl)2-(3H)-furanone (5d), 3,3-diphenyl-5-(4-ethoxy-
phenyl)-2(3H)-furanone (5e), 5-(4-chlorophenyl)-3,3-di-
phenyl-2(3H)-furanone (5f), 5-(4-cyanophenyl)-3,3-di-
phenyl-2(3H)-furanone (5g), and 5-(4-biphenylyl)-3,3-di-
phenyl-2(3H)-furanone (5h) have been examined. These
furanones 5b-h were prepared by the thermolysis of the
corresponding 1-aryl-3,4-diphenylbut-2-en-1,4-diones
10b-h.

Irradiation of 5b-h in benzene gave the corresponding
decarbonylated products 6b-h in high yields. The p-me-
thoxyacetophenone sensitized irradiation of 5b-h in benzene,

on the other hand, gave the corresponding 5-aryl-3,4-di-phenyl-2(5H)-furanones, 7b-h, the 3-arylphenanthro[9,10-c]fu-ran-1(3H)-ones, 9b-h and dimeric products, 10b-f.

Laser excitation (337.1 or 355 nm) of acetophenone in the presence of 5b-h generated the triplets of these fura-nones; the data concerning their absorption spectra and kinetic behaviour are presented. From the observed triplet lifetimes, the phenyl group migration rates have been esti-mated at $\leq 1 \times 10^6$ s^{-1} and it has been found that both ele-ctron-releasing and electron-withdrawing p-substituents on the aryl group at C-5 position slow down these reactions.

III.2   INTRODUCTION

Photochemical and thermal transformations of five-membered unsaturated lactones such as 2(3H)-furanones and 2(5H)-furanones have been investigated in detail.[1-25] Some of the major reaction pathways followed by these furanones under photochemical conditions include solvent addi-tion,[14,16,22,23] migration of aryl substituents[23] and dimerization.[19,25] In addition, 2(3H)-furanones undergo facile decarbonylation reaction leading to α,β-unsaturated carbonyl compounds.[4,5,9,10]

Photochemical transformations of several 2(3H)-fu-ranones have been reported recently from this laboratory.[26-30]

The two prominent pathways for the photoreactions of these
2(3H)-furanones are singlet-mediated decarbonylation, to
give α,β-unsaturated carbonyl compounds and electrocyclic
ring closure reactions of the stilbene moieties to give
4a,4b-dihydrophenanthrenes (Scheme III.1). Thus, tetra-
phenyl-2(3H)-furanone (1a) on irradiation in benzene or
methanol gave the decarbonylated product 2a in major amounts,
along with a small amount of the phenanthrofuranone 4a. In
contrast, the irradiation of 1b and 1c, under analogous
conditions, gave the phenanthrofuranones 4b and 4c respecti-
vely, as the only isolable products. Direct irradiation of
a triaryl substituted furanone such as 3,3,5-triphenyl-
2(3H)-furanone (5a) gave exclusively the decarbonylated
product 6a, whereas, the sensitized irradiation of 5a gave
a mixture of 3,4,5-triphenyl-2(5H)-furanone (7a) and 3-phenyl-
phenanthro[9,10-c]furan-1(3H)-one (9a). The formation of 7a
from 5a has been suggested to arise through a C-3 to C-4
phenyl migration followed by further reorganizations, whereas,
the phenanthrofuranone 9a has been shown to arise through the
further photoreactions of 7a.[28,29]

   The object of the present investigation has been to
examine the mechanistic details of the phototransformations
of some 3,3,5-triaryl-2(3H)-furanones and in particular to

Scheme III.1

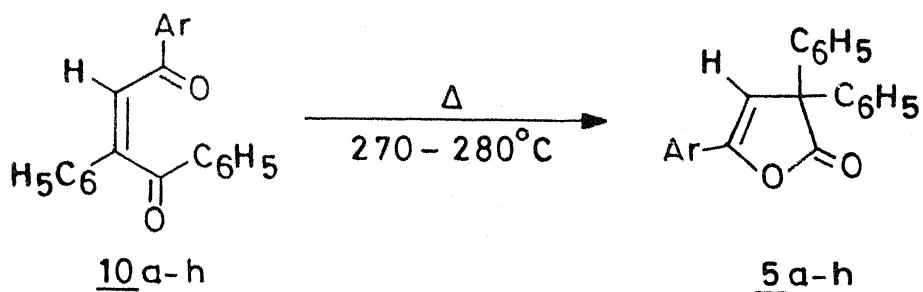a) R = C₆H₅

b) R = CH₃

c) R = CH₂C₆H₅
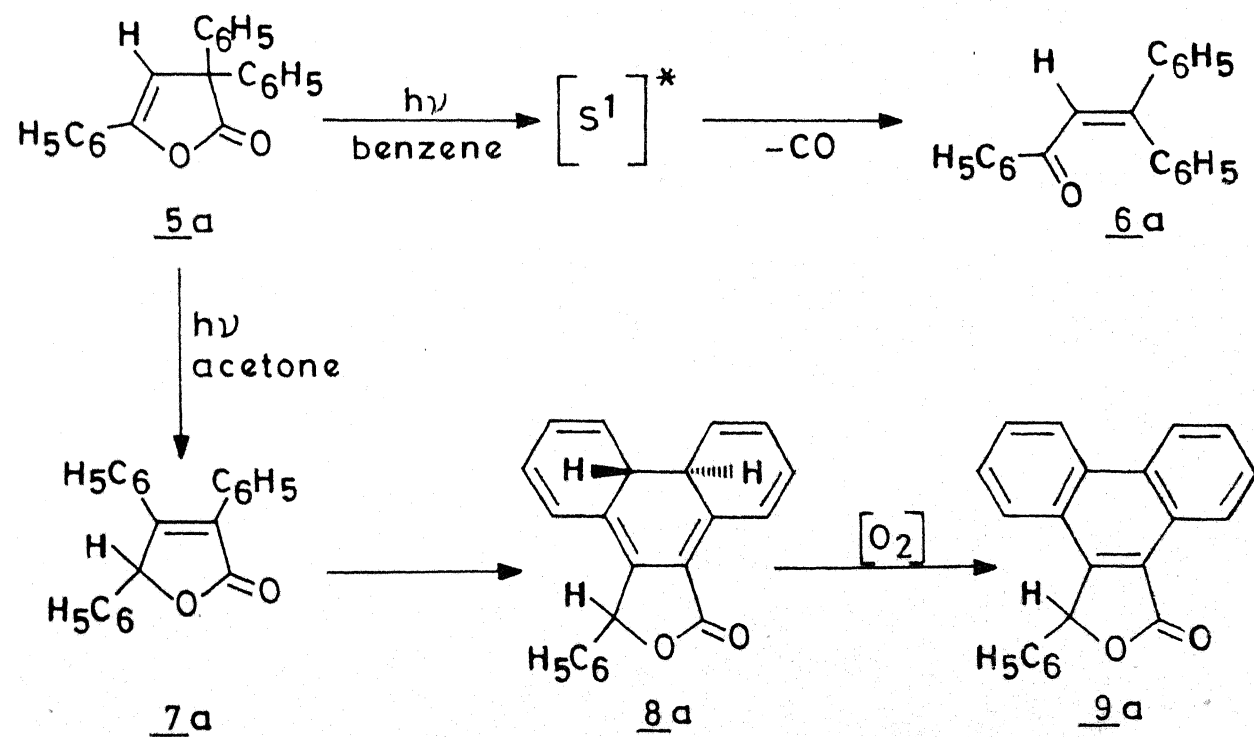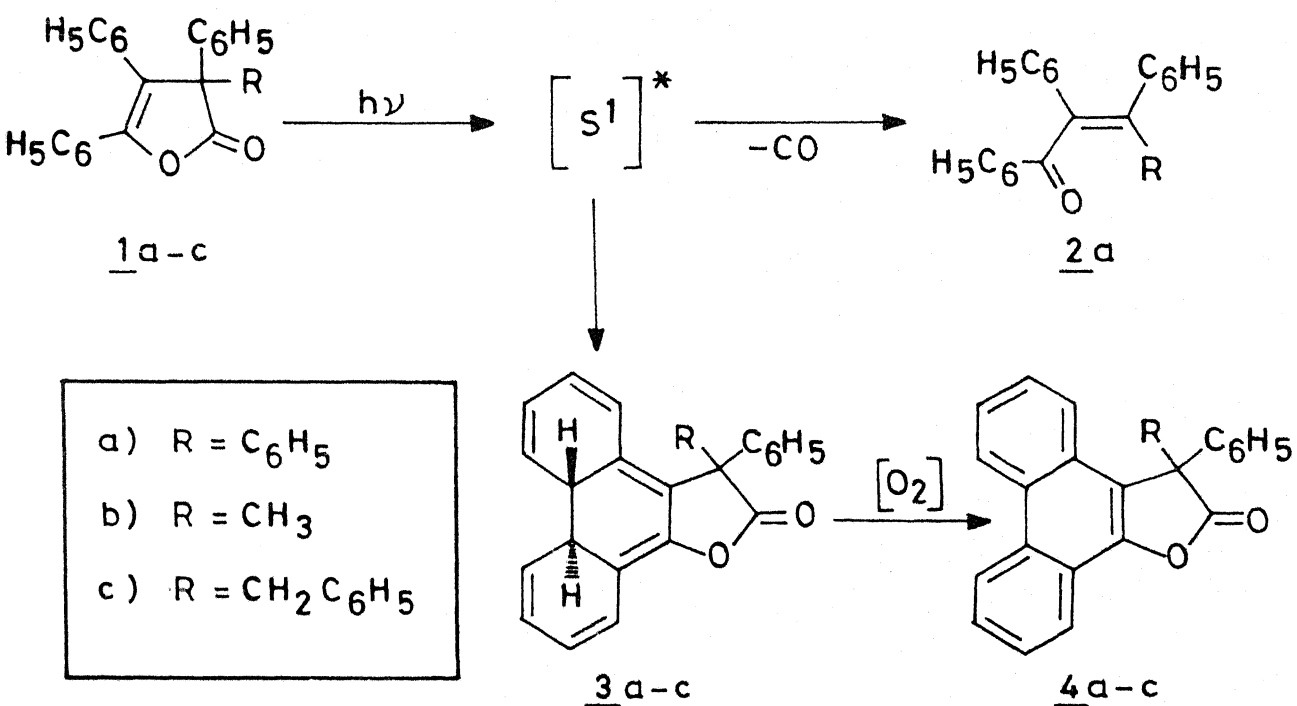
study the effect of different para substituents on the C-5
phenyl group (electron donating and electron withdrawing)
in stabilizing the intermediates involved in these rearrange-
ments. The 2(3H)-furanones that we have examined in this
connection include, 3,3-diphenyl-5-(4-methylphenyl)-2(3H)-fu-
ranone (5b), 3,3-diphenyl-5-(4-ethylphenyl)-2(3H)-furanone
(5c), 3,3-diphenyl-5-(4-methoxyphenyl)-2(3H)-furanone (5d),
3,3-diphenyl-5-(4-ethoxyphenyl)-2(3H)-furanone (5e),
5-(4-chlorophenyl)-3,3-diphenyl-2(3H)-furanone (5f),
5-(4-cyanophenyl)-3,3-diphenyl-2(3H)-furanone (5g), and
5-(4-biphenylyl)-3,3-diphenyl-2(3H)-furanone (5h).

III.3 RESULTS AND DISCUSSION

III.3.1 Preparation of Starting Materials. The
5-aryl-3,3-diphenyl-2(3H)-furanones 5b-h, that we have
examined in the present studies were prepared by the neat
heating of the appropriate 1-aryl-3,4-diphenylbut-2-en-
1,4-diones 10b-h[1,2] (Scheme III.2). The structures of 5b-h
have been established on the basis of analytical results,
spectral data and comparison with authentic samples prepared
by well-defined routes.

III.3.2 Preparative Photochemistry and Product Identi-
fication. Direct irradiation of a benzene solution of 5b

Scheme III.2

$$\underline{10}\,a\text{-}h \xrightarrow[\substack{270-280°C}]{\Delta} \underline{5}\,a\text{-}h$$

a)	Ar = C_6H_5
b)	Ar = $C_6H_4CH_3$-p
c)	Ar = $C_6H_4C_2H_5$-p
d)	Ar = $C_6H_4OCH_3$-p
e)	Ar = $C_6H_4OC_2H_5$-p
f)	Ar = C_6H_4Cl-p
g)	Ar = C_6H_4CN-p
h)	Ar = $C_6H_4C_6H_5$-p

gave the decarbonylated product, 3,3-diphenyl-1-(4-methyl-phenyl)-prop-2-en-1-one (6b) in a 93% yield. Likewise, the irradiation of 5c-h, under analogous conditions, gave the corresponding decarbonylated products, 6c-h in yields ranging between 87-96% (Scheme III.3).

In contrast, the p-methoxyacetophenone sensitized irradiation of 5b in benzene gave a mixture of 3,4-diphenyl-5-(4-methylphenyl)-2(5H)-furanone (7b, 34%), 3-(4-methyl-phenyl)-phenanthro[9,10-c]furan-1(3H)-one (9b, 18%), the dimer 11b (11%), and the unchanged 5b (23%) (Scheme III.3). Similarly, irradiation of 5c, under analogous conditions, gave a mixture of the phenanthrofuranone 9c (44%), the dimer 11c (17%), and the unchanged 5c (17%). The sensitized irradiation of 5d in benzene also gave a mixture of the corresponding 2(5H)-furanone 7d (19%), the phenanthro-furanone 9d (9%), the dimer 11d (34%), and the unchanged 5d (30%), whereas, 5e under analogous conditions gave the dimer 11e (61%) as the major product; small amounts of the 2(5H)-furanone 7e (12%), the phenanthrofuranone 9e (6%), and the unchanged 5e (11%) could also be isolated. Likewise, the sensitized irradiation of 5f gave a mixture of the 2(5H)-furanone 7f (39%), the phenanthrofuranone 9f (9%), the dimer 11f (9%), and the unchanged 5f (29%), whereas the

Scheme III.3
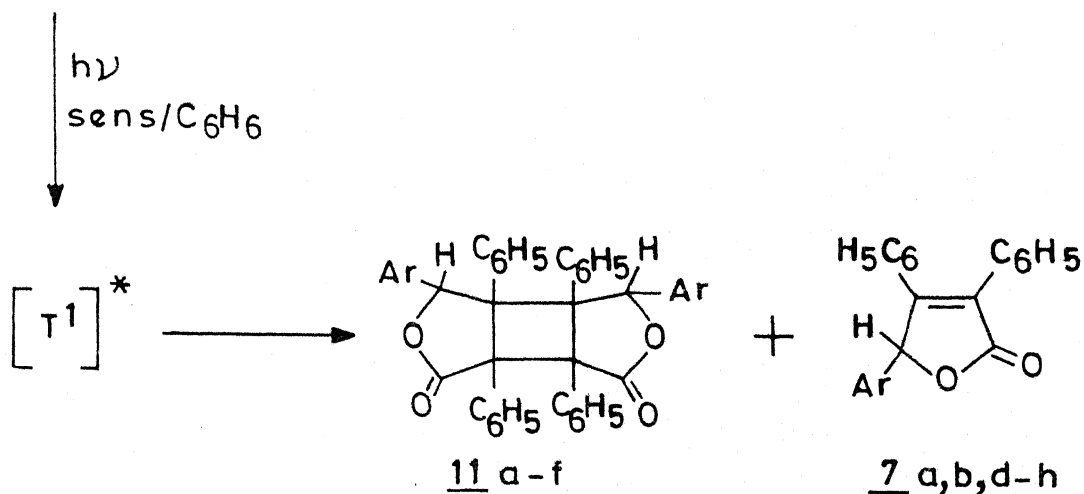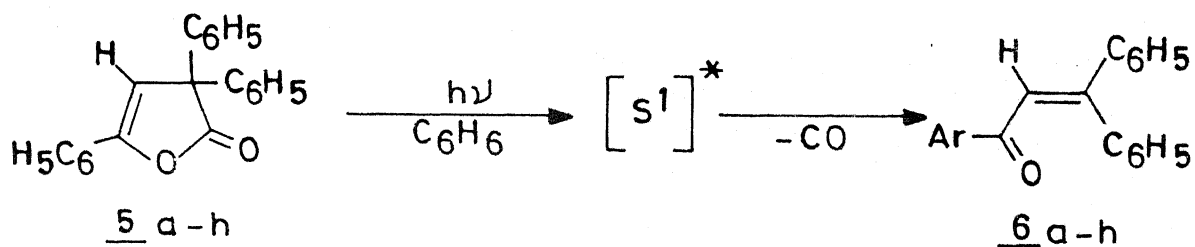
a) Ar = C_6H_5

b) Ar = $C_6H_4CH_3$-p

c) Ar = $C_6H_4C_2H_5$-p

d) Ar = $C_6H_4OCH_3$-p

e) Ar = $C_6H_4OC_2H_5$-p

f) Ar = C_6H_4Cl-p

g) Ar = C_6H_4CN-p

h) Ar = $C_6H_4C_6H_5$-p
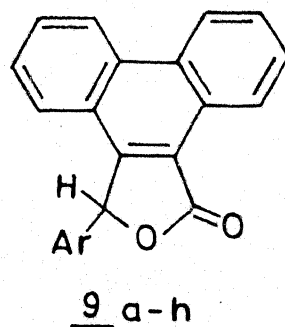
irradiation of 5g, under analogous conditions, gave a mixture of the 2(5H)-furanone 7g (52%), the phenanthrofuranone 9g (10%), and the unchanged 5g (18%). As compared to the facile reactions of 5b-g, the reaction of 5h under sensitized irradiation was quite sluggish. Thus, prolonged irradiation of 5h (6 h) gave a mixture of the 2(5H)-furanone 7h (12%) and the phenanthrofuranone 9h (40%); considerable amount of the unchanged 5h could be isolated (38%) even under these conditions. Details of the product yields and percentage recovery of the unchanged starting materials from steady-state irradiation of 5b-h in benzene, under various conditions, are given in Table III.1. The structures of all the photoproducts, obtained from the irradiations of 5b-h, were arrived at on the basis of analytical results, spectral data and comparison with authentic samples, wherever possible.

To examine whether the phenanthrofuranones 9a-h, formed in the sensitized irradiations of 5a-h, arise through the subsequent photoreactions of the initially formed 2(5H)-furanones 7a-h, we have studied the photoreactions of two representative examples such as 7b and 7e. Thus, the direct irradiation of a benzene solution of 7b for 4 h gave a 90% yield of the phenanthrofuranone 9b. Similarly, the irradiation of 7e, under analogous conditions, gave a 89% yield of 9e.

able III.1   Product Distribution in the Irradiation of 5-Aryl-
3,3-diphenyl-2(3H)-furanones (5a-h) in Degassed
Benzene

ubstrate	direct irradiation			sensitized irradiation				
	time, h	products, %		time, h	products, %			
		6	5		7	9	11	5
a	9[a]	87[a]	–	2	48	9	9	23
b	6	93	–	2	40	18	12	23
c	6	94	–	2	–	44	17	17
d	6	96	–	2	19	9	34	30
e	6	95	–	2	12	6	61	10
f	6	94	–	2	39	16	9	29
g	6	87	6	2	52	10	–	18
h	6	92	–	6	12	40	–	38

Data taken from references 26-29.

An attempt has also been made to study the solvent effects, if any, in the triplet-sensitized transformations of the 3,3,5-triaryl-2(3H)-furanones 5a-h. Thus, the irradiation of a representative substrate such as 5b in hexane under p-methoxyacetophenone sensitization, for example, gave the photodimer 11b (77%) as the major product; a small amount of the phenanthrofuranone 9b (11%) could also be isolated from this reaction. In contrast, the irradiation of 5b in acetonitrile, under analogous conditions, did not give any of the photodimer 11b; only a mixture of the rearranged 2(5H)-furanone 7b (25%) and the phenanthrofuranone 9b (31%) could be isolated, along with some unchanged starting material (5b, 29%). Sensitized irradiation of 5b, in methanol, on the other hand gave exclusively the methanol addition product, cis-3,4-diphenyl-5-methoxydihydro-5-(4-methyl-phenyl)-2(3H)-furanone (16b, 83%). The methanol adduct 16b alone could be isolated when the sensitized irradiation of 5b was carried out in a mixture (9:1) of benzene and methanol. Similarly, the sensitized irradiation of the 2(3H)-furanone 5g in methanol gave cis-5-(4-cyanophenyl)-3,4-diphenyl-5-methoxydihydro-2(3H)-furanone (16g, 62%). The structures of both 16b and 16g were established on the basis of analytical results, spectral data and literature precedents.[23,28,29]

In order to ascertain the spin multiplicity of the excited state species involved in the phototransformations of the 3,3,5-triaryl-2(3H)-furanones (5b-h) under investigation, an attempt was made to study the role of a triplet quencher such as piperylene in some of these reactions. Thus, the direct irradiation of a benzene solution of 5b, containing excess of piperylene, gave the decarbonylation product 6b in a 95% yield, indicating thereby that the photodecarbonylation reaction is singlet mediated.

III.3.3 Laser Flash Pholysis Studies.[31] Each of the 2(3H)-furanones 5a-h is characterized by a strong, low energy absorption system at 250-330 nm(λ_{max}'s = 274-287 nm, ε_{max}'s = (18-30) x 10^3 M^{-1} cm^{-1}). This absorption extends up to 320-340 nm, beyond which it is negligible at millimolar substrate concentrations. Thus, while it was convenient to photoexcite the substrates 5a-h via direct absorption of 308 nm laser pulse, the triplet sensitization experiments were carried out through the laser excitation (337.1 or 355 nm) of aromatic ketones, in the presence of 5-20 mM concentrations of 5a-h. In the present studies, we have used benzophenone, acetophenone and p-methoxyacetophenone as sensitizers. The excitation transfer from the triplets of the ketones ($E_T \geq 69$ kcal mol^{-1})[32] to the styryl moiety

$(E_T \sim 62 \text{ kcal mol}^{-1})$[32] of the 2(3H)-furanones were expected
to occur in a diffusion controlled manner. A more precise
knowledge of the location of the triplet energies (E_T) of
5a-h was obtained from the quenching behaviours of their
triplets (see later).

(a) Direct Excitation of 2(3H)-Furanones. The 308 nm
laser flash excitation of benzene solutions of 5b,d-h result-
ed in pronounced absorbance changes at 300-400 nm. The photo-
products responsible for these absorbance changes were found
within nanoseconds of the laser pulse and showed practically
no sign of decay over the longest time scale (150 µs) of
observation. The transient absorption spectra and the kinetic
traces in the case of 5d and 5g are presented in Figure III.1.
Based on the permanent nature of the absorbance changes and
their spectral similarity with the difference absorption
spectra between the 1,3,3-triaryl-prop-2-en-1-ones 6b,d-h and
the corresponding 2(3H)-furanones 5b,d-h (see Figure III.1),
we attribute these absorbance changes to prompt two-bond
photocleavage resulting in the loss of carbon monoxide.

There was no indication of the formation of triplets
upon 308 nm laser pulse excitation of the 2(3H)-furanones
5b,d-h in benzene or methanol. Based on the triplet extin-
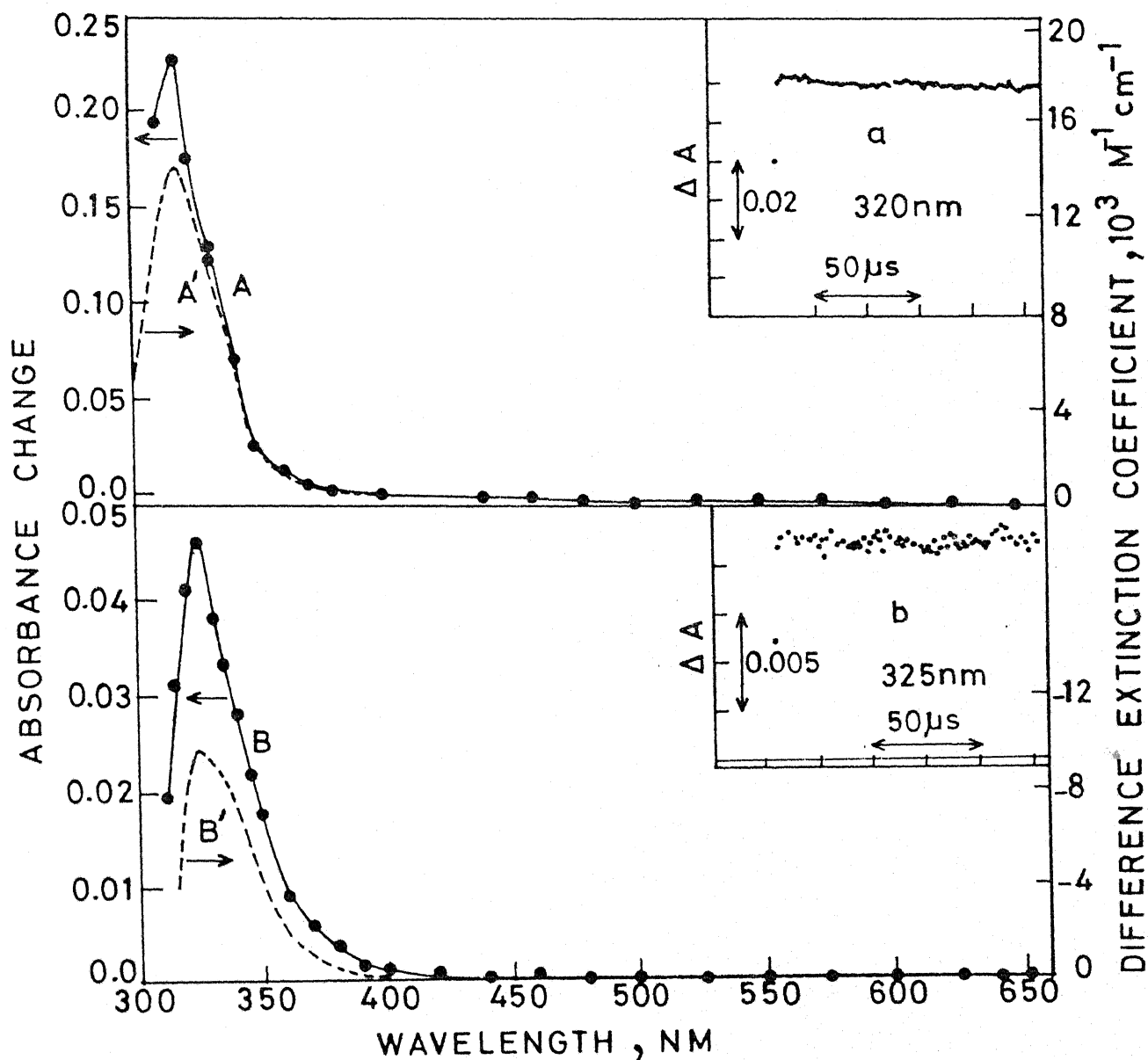ction coefficients, estimated by energy-transfer technique in

Figure III.1   Absorbance changes following 308 nm laser flash photolysis of (A) 5d and (B) 5g in benzene.   The dotted curves A' and B' are difference absorption spectra in benzene for pairs (5d, 6d) and (5g, 6g), respectively.   Insets: kinetic traces for transient decay at the wavelenghts indicated.

benzene (see later), ϕ_T's were estimated at well below 1%.
For 5g and 5h in methanol saturated with potassium iodide,
transient species characterized by spectral and kinetic
behaviours similar to those of the triplets of these systems
(as observed under acetophenone or p-methoxyacetophenone tri-
plet sensitization, see later) were formed under direct 308 nm
laser excitation. Similar observations regarding heavy-atom
induced intersystem crossing were also made for 5g and 5h in
benzene in the presence of ethyl iodide (0.5 M). With the
other 2(3H)-furanones, the enhancement of triplet yield upon
saturating their methanol solutions with potassium iodide was
negligible.

Employing benzophenone triplet formation in acetonitrile
for actinometry ($\phi_T = 1.0$, $\varepsilon_{max}^T = 6.5 \times 10^3$ M^{-1} cm^{-1} at
520 nm),[33] and using ground-state extinction coefficients of
the products 6b,d-h, we have estimated the quantum yields of
decarbonylation (ϕ_P) of 5b,d-h in methanol. In these experi-
ments, the solutions were optically matched at the laser exci-
tation wavelength (absorbance = 0.2 at 308 nm in 2 mm cells)
and the absorbance changes as a result of laser excitation
were noted at 320-330 nm. The ϕ_P data are presented in
Table III.2. The ϕ_P's of 5g and 5h are substantially smaller
than those of the other 2(3H)-furanones. The variation of ϕ_P

Table III.2   Photoproduct Absorption Maxima and Yields of

5-Aryl-3,3-diphenyl-2(3H)-furanones (5a-h)

in Methanol (λ_{ex} = 308 nm)

substrate	λ_{max}^{P}, nm[a]	Φ_P[b]
5a	310[c]	0.30[c]
5b	305	0.23
5c	–	–
5d	315	0.20
5e	315	0.21
5f	305	0.26
5g	325	0.10
5h	320	0.12

[a] ± 5 nm; these maxima correspond to the difference absorption spectra. [b] ± 20%; corresponds to decarbonylation products. [c] Data taken from references 28 and 29.

upon going from degassed to air-saturated methanol solutions were well within experimental errors.

(b) <u>Triplets of 2(3H)-Furanones</u> <u>5b,d-h</u>. <u>Sensitization</u> <u>by Aromatic Ketone Triplets</u>. Transient absorption spectra and decay kinetics attributable to the triplets of <u>5b,d-h</u> were investigated by 337.1 nm laser flash photolysis of acetophenone in benzene in the presence of 10-15 mM <u>5b,d-h</u>. Representative triplet absorption spectra and decay profiles are shown in Figure III.2. The data concerning absorption maxima (λ_{max}^{T}) and lifetimes (τ_T) are compiled in Table III.3. Previous studies[26-29] on related 3,3,5-triaryl-2(3H)-furanones have revealed that the quenching of their triplets by the respective ground states (i.e., self quenching) is insignificant ($k_{SQ}^{T} \leq 10^7$ M^{-1} s^{-1} in benzene). This aspect was not pursued in any detail in the present cases; the reported triplet lifetimes (τ_T, Table III.3) correspond to a given concentration (12.5 mM for benzene and 10 mM for methanol). τ_T data in methanol were obtained with <u>p</u>-methoxyacetophenone as triplet donor (λ_{ex} = 337.1 nm); the hydrogen abstraction by <u>p</u>-methoxyacetophenone triplet from methanol is far less efficient than that by acetophenone triplet.
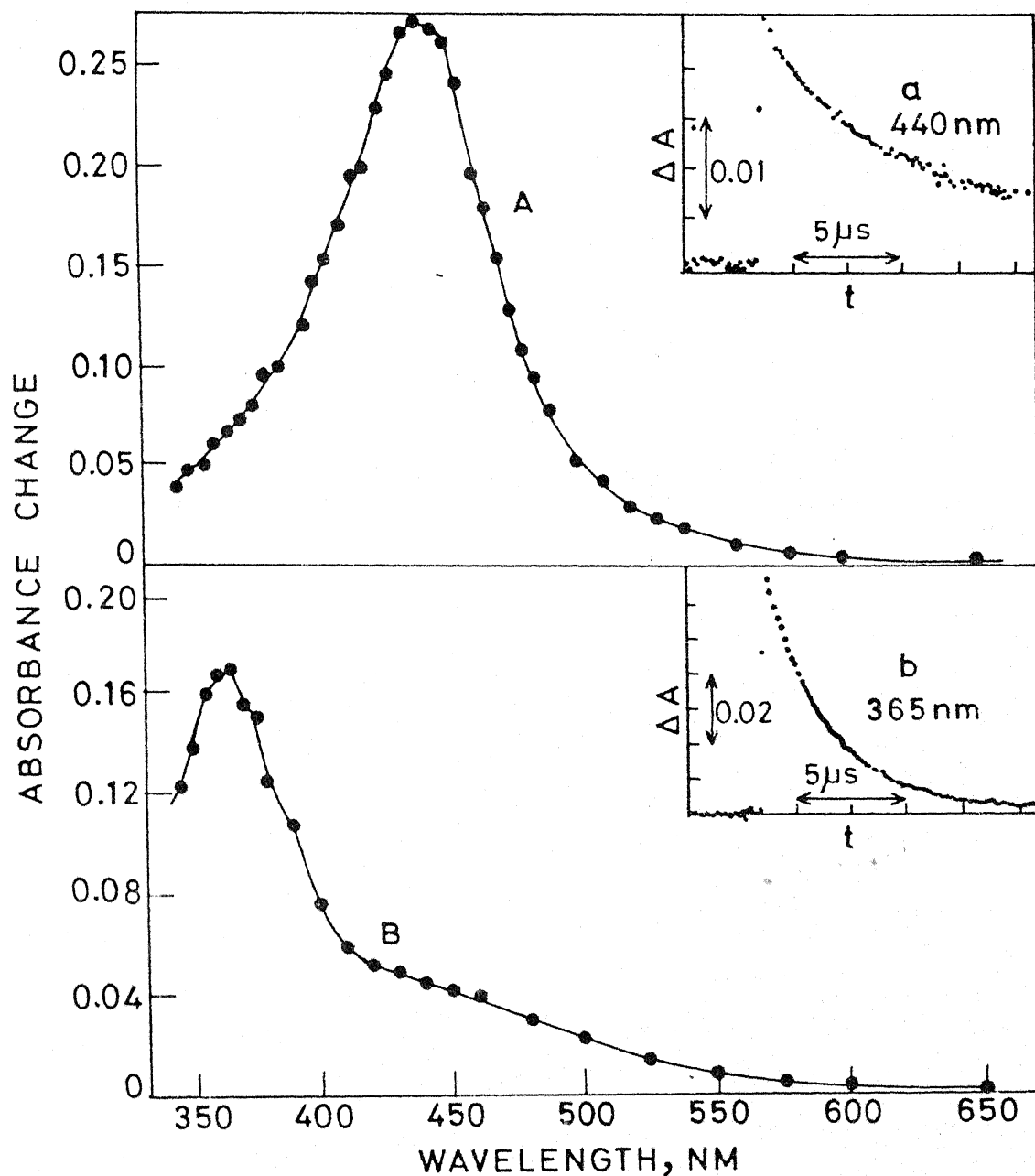
Figure III.2   Triplet-triplet absorption spectra of (A) 5g and (B) 5h in benzene following acetophenone sensitization. Insets: kinetic traces for triplet decay at the wavelengths indicated.

In order to confirm the triplet identification of the transients observed under aromatic ketone triplet sensitization, their quenching behaviours towards oxygen, ferrocene and 2,5-dimethyl-2,4-hexadiene (DMHD) were studied in detail. The bimolecular rate constants (k_q^T) for triplet quenching by ferrocene and DMHD were obtained from the slopes of the linear plots of observed pseudo-first-order rate constants for triplet decay vs. quencher concentrations. With oxygen as quencher, k_q^T data were obtained from single-concentration measurements, i.e., from the observed triplet decay rates in air-saturated benzene. The k_q^T data are compiled in Table III.3.

The extinction coefficients of triplet-triplet (T-T) absorptions of 5b,d-h were obtained by experiments in which benzene solutions of benzophenone (absorbance = 2.0 at 355 nm in 2 mm cells) containing 20-30 mM 5b,d-h were flash photolyzed. The end-of-pulse absorbance due to benzophenone triplet ($\varepsilon_{max}^T = 7.6 \times 10^3$ M^{-1} cm^{-1} at 532 nm)[34] in the absence of an acceptor was compared with the absorbances due to the triplets of 5b,d-h observed at 360-440 nm upon laser excitation of benzophenone solutions containing high concentrations of 5b,d-h. Under the conditions of our experiments, $\geq$95% of benzophenone triplets were quenched by energy transfer to the 2(3H)-furanones and $\leq$2% of the laser photons at 355 nm were

Table III.3   Absorption Spectral and Kinetic Properties of the
Triplets of 5-Aryl-3,3-diphenyl-2(3H)-furanones
(5a–h) in Benzene at 295 K

substrate	λ_{max}^{T}[a], nm	ε_{max}^{T}[b], $10^3 M^{-1}cm^{-1}$	τ_T[c], μs	k_q^{T}, $10^9 M^{-1} s^{-1}$[d]		
				O_2	DMHD	ferrocene
5a[e]	335	13	0.92 (1.03)	1.6	0.98	5.0
5b	350	15	1.40 (1.90)	1.7	0.84	4.5
5c	–	–	–	–	–	–
5d	355	13	1.90 (2.60)	2.3	0.73	4.6
5e	360	–	1.80 (1.80)	2.2	0.73	3.6
5f	350	15	2.10 (2.10)	1.4	0.93	4.2
5g	365	21	3.00 (3.40)	1.1	1.20	5.0
5h	440	39	7.70 (17.00)	1.4	0.40	5.1

[a] ± 5 nm. [b] ± 20% . [c] ± 15%; the data in parenthesis are in methanol; substrate concentrations were 12.5 mM in benzene and 8-10 mM in methanol. [d] ± 15%; k_q^{T}'s for oxygen were calculated from observed triplet decay rate constants in air-saturated and degassed solutions. [e] Data taken from references 26-29.

absorbed by the 2(3H)-furanones 5b,d-h. The ε_T data obtained in this manner for wavelengths which were not T-T absorption maxima were then used to calculate ε_{max}^{T}'s (see Table III.3), based on previously obtained, relatively complete T-T absorption spectra that included the maxima.

(c) Triplet Yield Enhancement and Fluorescence Quenching by Iodide Ion. As mentioned earlier, the triplet formation in the case of 5g and 5h is effected by the presence of heavy atoms. This aspect was pursued in detail using iodide ion as singlet quencher in methanol. Not surprisingly, among the 2(3H)-furanones 5b,d-h, 5g and 5h are the only systems for which weak fluorescence were observed under steady-state lamp excitation. The fluorescence spectra in methanol are presented in Figure III.3. The quantum yields of fluorescence in methanol were estimated to be 0.014 and 0.009 for 5g and 5h, respectively. Upon oxygen saturation, the intensity of fluorescence from a methanol solution of 5h remained practically unchanged, while that in the case of 5g displayed a marginal decrease ($\sim$8%). Based on a typical value of 2×10^{10} M^{-1} s^{-1} for diffusion-controlled singlet quenching by oxygen in methanol,[35,36] the singlet excited state lifetimes for 5g,h were estimated at $\geq$0.5 ns.

The effect of varying concentrations of iodide ion
(0-0.2 M) on fluorescence intensity (steady-state), triplet
yield and decarbonylation yield of 5g and 5h were investiga
ted. Figure III.4, parts A and B show the Stern-Volmer plo
for fluorescence quenching of 5g and 5h by iodide ion in
methanol. From the slopes of these linear plots, the fluor
cence quenching constants k_{SV}^{F} were estimated to be 2 ± 0.5
and 1 ± 0.5 M^{-1} for 5g and 5h, respectively. Based on the
parallel photoprocesses, represented by equations III.1-
III.5, originating from the lowest singlet (S_1), equa-
tions III.6-III.8 could be easily deduced for the quenching
of fluorescence and photochemistry and enhancement of tripl

$$S_1 \longrightarrow S_0 + h\nu_F \qquad\qquad (III.1)$$

$$S_1 \rightsquigarrow S_0 \qquad\qquad (III.2)$$

$$S_1 \longrightarrow P \qquad\qquad (III.3)$$

$$S_1 + I^- \longrightarrow T_1 + I^- \qquad\qquad (III.4)$$

$$S_1 + I^- \longrightarrow S_0 + I^- \quad \text{or other} \qquad (III.5)$$
$$\text{products}$$
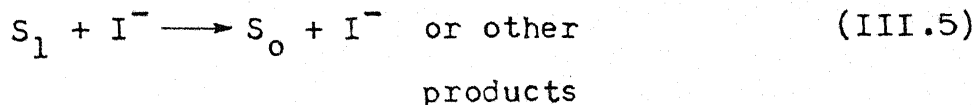
formation. In equations III.6-III.8, I = steady-state flu-
orescence intensity, ΔA = absorbance change as a result of

laser pulse excitation, K_{SV} = Stern-Volmer constant,
δ_T = fraction of quenching events that result in triplet
formation. In the absence of complications, one would
expect K_{SV}^F, K_{SV}^P and K_{SV}^T to be identical. Figure III.4,

$$\frac{I_F^O}{I_F} = 1 + K_{SV}^F \; [I^-] \qquad\qquad (III.6)$$

$$\frac{\Delta A^O}{\Delta A_P} = 1 + K_{SV}^P \; [I^-] \qquad\qquad (III.7)$$

$$\frac{1}{\Delta A_T} = Const. \; \frac{1}{\delta_T} \; [1 + \frac{1}{K_{SV}^T \; [I^-]}] \qquad\qquad (III.8)$$

parts A' and B' show the double reciprocal plots for tri-
plet formation based on equation III.8. The absorbance
changes (ΔA_T) due to triplets were monitored at 380 and
435 nm for 5g and 5h, respectively, following 337.1 nm laser
flash photolysis of their methanol solutions (absorbance =
0.2 in 2 mm cells at 337.1 nm) containing varying amounts of
iodide ion. The slopes-to-intercept ratios of the plots in
Figure III.4, parts A' and B' gave 3 ± 1 and 2 ± 1 for K_{SV}^T for
5g and 5h, respectively. In view of the large experimental
errors, K_{SV}^F and K_{SV}^T data should be considered to agree
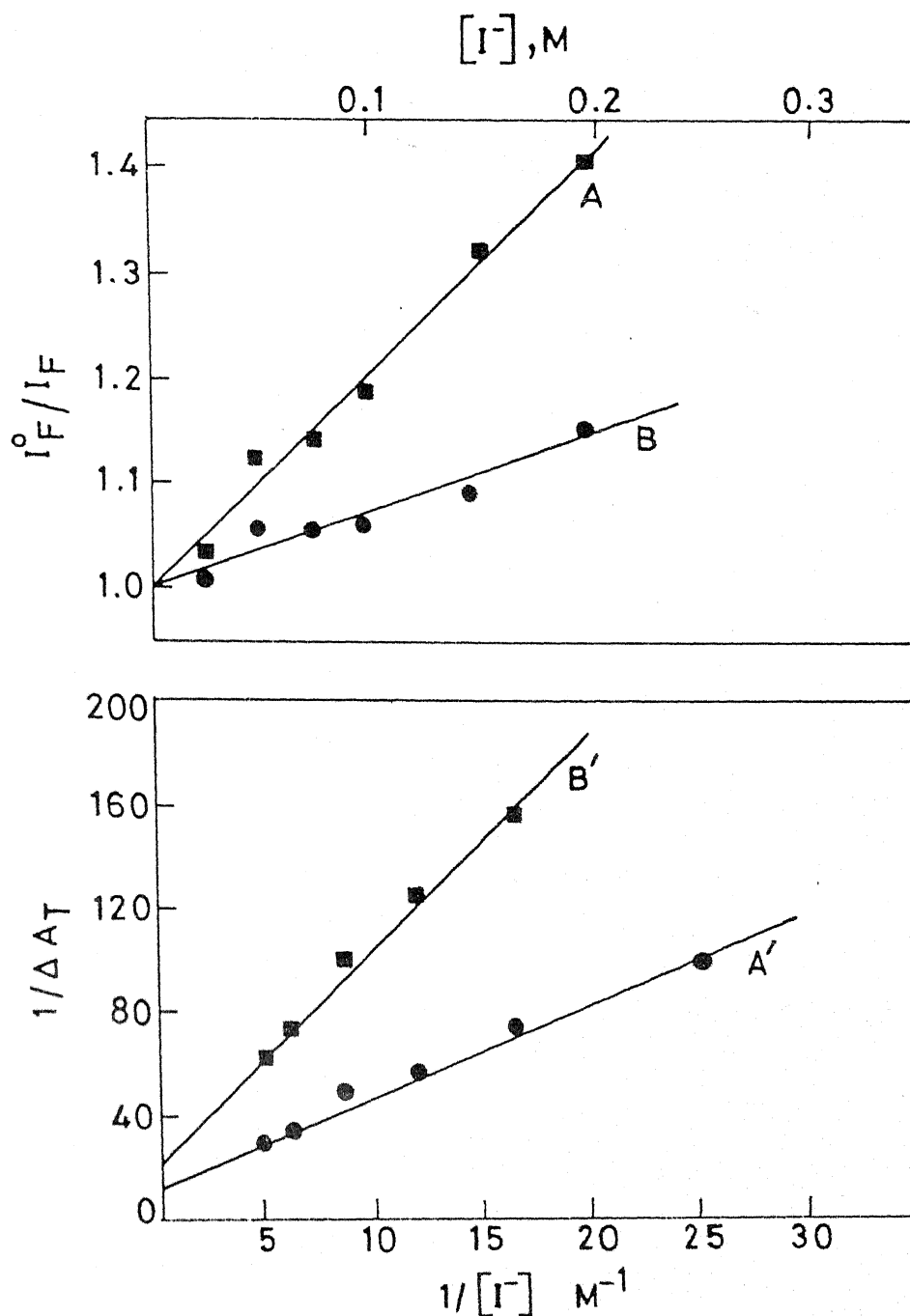with each other. Furthermore, comparison of the reciprocals

Figure III.4 Stern-Volmer plots, based on equation III.6 for fluorescence quenching of (A) 5g and (B) 5h and double reciprocal plots based on equation III.8 for triplet yield enhancement of (A') 5g and (B') 5h in methanol (quencher: iodide ion)

of the intercepts of the plots in Figure III.4, parts A' and
B' (i.e., ΔA_T's at infinite concentration of iodide ion) with
absorbance changes due to benzophenone triplet in optically
matched solutions of benzophenone in acetonitrile led to
estimates of 0.8 and 0.3 for δ_T in the case of 5g and 5h,
respectively. In calculating δ_T, we have assumed that λ_{max}^T's
of 5g and 5h in methanol are the same as those in benzene
(Table III.2).

In the case of 5h, the triplet does not absorb signifi-
cantly at the wavelength maximum of absorbance change (330 nm)
due to photodecarbonylation. Therefore, the relative change
in the latter as a function of the concentration of iodide ion
could be monitored without difficulty. However, the magni-
tudes of decrease in ΔA_p as a result of quenching by iodide
ion were small and within experimental uncertainties of the
absorbance change measurement. We still could observe 10-15%
decrease in ΔA_p at the highest concentration of iodide ion
used (i.e., 0.2 M). This extent of quenching of product for-
mation is in agreement with that observed for fluorescence.
In the case of 5g, the contribution of triplet absorption at
short wavelengths (320-330 nm) is insignificant; the absor-
bance change due to decarbonylation product had to be deter-
mined following the completion of triplet decay (over ~15 μs)

after the laser pulse). A comparison of ΔA_p's (monitored
at 325 nm) in the absence and 0.2 M concentration of iodide
ion shows that the decrease (~10%) in ΔA_p as a result of
quenching by iodide ion is less than that expected from the
extent of fluorescence quenching (30%) under the same condi-
tion. This complication, however, could be recognized in
terms of the contribution of the product(s) of the decay of
the triplet, at the short-wavelength region.

I.3.4 <u>Discussion</u>. The triplet mediated photorearrange-
ment of the 2(3H)-furanones <u>5a-h</u> to the 2(5H)-furanones <u>7a-h</u>
could be explained in terms of the pathway shown in
Scheme III.4.[29] The triplet state of the 2(3H)-furanone could
be viewed as a diradical intermediate <u>12</u>, in which one of the
C-3 phenyl groups could migrate to the C-4 position, perhaps,
through a bridged transition state, to give the rearranged
diradical intermediate <u>13</u>. Electron demotion from <u>13</u> will
lead to the zwitterionic intermediate <u>14</u>(A,B), which will then
undergo hydride shift to give the corresponding 2(5H)-furanones
(<u>7</u>). The involvement of zwitterionic intermediates (<u>14</u>) in the
phototransformations of <u>5</u> has been confirmed through the iso-
lation of the methanol adducts <u>16b</u> and <u>16g</u>, when the sensitized
irradiation of <u>5b</u> and <u>5g</u>, respectively, were carried out in
methanol (Scheme III.4). The formation of the phenanthrofura-
nones <u>9a-h</u> in the sensitized irradiation of <u>5a-h</u>, however, can

Scheme III.4
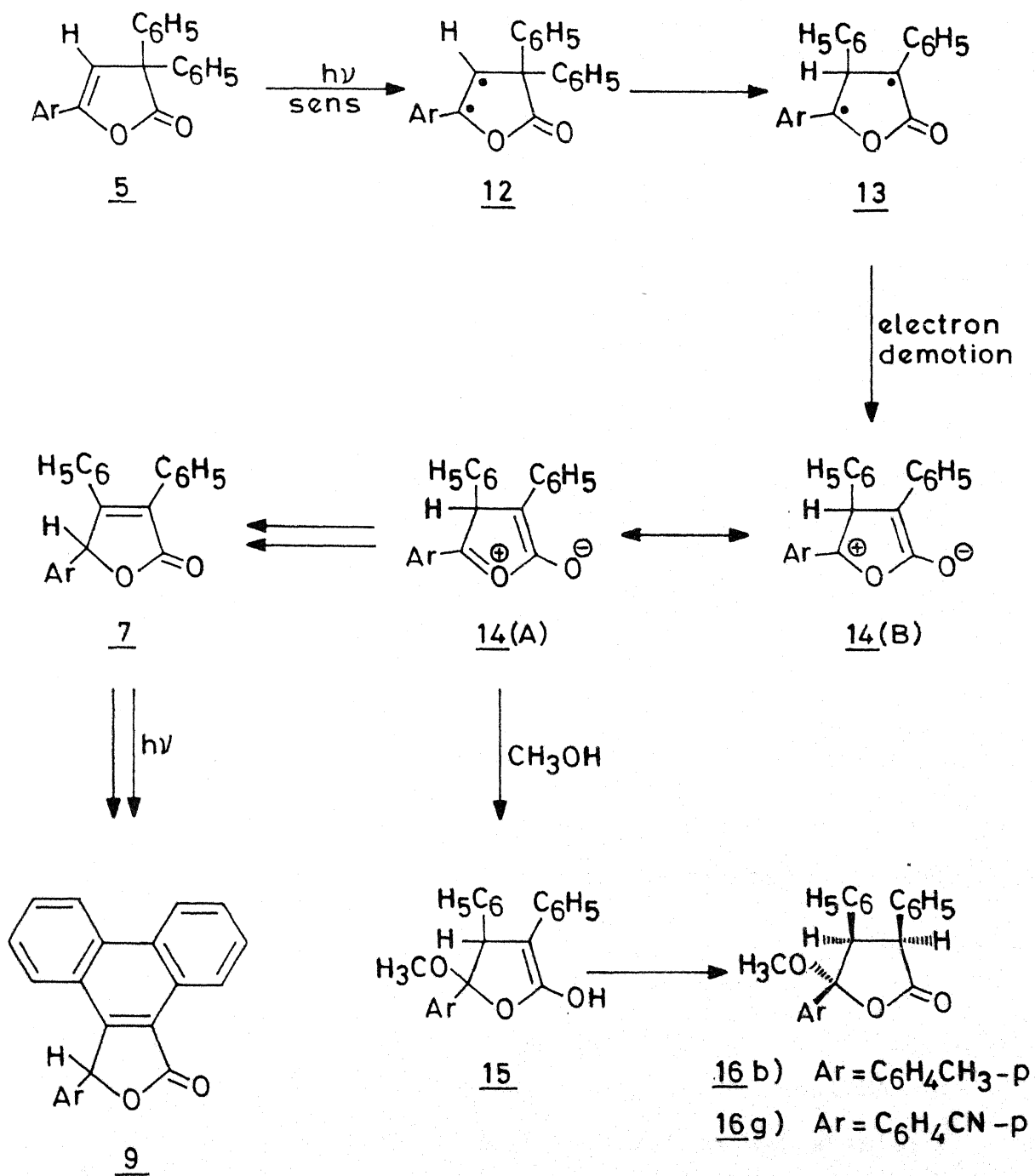
be understood in terms of the further transformations of the initially formed 2(5H)-furanones 7a-h (Scheme III.4).

If zwitterionic intermediates such as 14 are involved in the triplet-mediated transformations of 2(3H)-furanones (5a-h) to the corresponding 2(5H)-furanones (7a-h), then it would be of interest to examine the effect of different para substituents in the C-5 phenyl group, on these rearrangements. From the product yields and triplet lifetime data presented in Tables III.1 and III.3, it is not very clear whether any definite correlation exists between the para substituents of the C-5 phenyl group and the product yields, reflecting C-3 to C-4 phenyl group migration. This is not entirely surprising since in the suggested pathway (Scheme III.4), the zwitterionic intermediate 14 (or the development of charge at the C-5 position of the furanone ring) is invoked only after the migration of the aryl group from C-3 to C-4 position has occurred. However, it may be noted that the presence of electron-releasing groups at the para position of the C-5 phenyl group generally favoured the formation of the dimeric product, the reason for which is not fully understood yet. It has been observed that the product composition in the phototransformations of 2(3H)-furanones has been considerably affected by the nature of the solvent employed. Thus, it has been observed that in non-polar solvents such as hexane, dimerization was a major

reaction pathway, whereas in polar solvents such as acetonitrile, the dimerization was totally suppressed. These observations are in agreement with earlier reports on the photochemistry of related systems.[25-29]

Based on the consideration that the quantum yields of the phenyl group migration process from the triplet states are necessarily ≥ 1, we conclude that the reciprocals of the observed triplet lifetimes represent the upper limits of the migration rates. From the τ_T data compiled in Table III.3, these limits of migration rates are shown to range from 1.1×10^6 s^{-1} (5a in benzene) to 6.0×10^4 s^{-1} (5h in methanol). Interestingly, compared to the unsubstituted system 5a, both electron-releasing (e.g., methoxy) and electron-withdrawing (e.g., cyano) substituents at the p-position of C-5 phenyl group cause lengthening of triplet lifetimes. The radical center at C-5 position in 13, produced as a result of C-3 to C-4 phenyl group migration is expected to be stabilized by both electron-releasing and withdrawing substituents at the p-position of the aryl group at this position. Thus, one would expect an enhancement of the migration rate upon substitution by these groups at this position. Since, in practice, we observe a decrease in the triplet decay rates ($1/\tau_T$) upon substitution, we conclude

that the enhancement (if any) in the migration rates is more than compensated for by the decrease in the intersystem crossing rates, $T_1 \rightsquigarrow S_0$. More plausibly, the migration rates are slowed down upon introduction of the p-substituents. In particular, for 5h, the marked decrease in the migration rate is reflected in the sluggishness of product formation under the steady-state irradiation with p-methoxyacetophenone sensitization.

Since the rate constants for triplet quenching (k_q^T, Table III.3) by DMHD are well below the limits of diffusion control, the triplet energies of the 2(3H)-furanones are lower than, but close to, E_T of DMHD (59 kcal mol^{-1}).[32] We should note that the observed quenching can also be in part due to non-energy-transfer interactions, e.g., 2+2 addition and oxetane formation. In fact, the effect in terms of decreasing k_q^T from electron-releasing substituents (p-methoxy) and in terms of increasing k_q^T from electron-withdrawing substituents (p-cyano) suggests the importance of charge-transfer interaction of the triplets with electron-rich diene. The most significant change (i.e., decrease) in k_q^T is noted with 5h; this is probably, in part, a reflection of the relatively large lowering of E_T upon p-phenyl substitution. Note that the T-T absorption maximum of 5h is also conspicuously red-

shifted, suggesting a pronounced effect from the aromatic substituent on the electronic make-up of the triplet.

The substituent effect is also evident, to a certain extent, in the rate constants for triplet quenching by oxygen (Table III.3). While these are all close to $1/9$ k_{diff} (i.e., the spin-statistically limited value, expected for energy-transfer quenching),[37] there is a small but gradual increase in these rates as one proceeds from electron-withdrawing substituents to electron-releasing ones. Such a trend, not uncommon for oxygen quenching, has been observed previously for series of substituted acetophenones and benzophenones[38] and probably implies a certain degree of charge-transfer interaction.

The singlet-mediated decarbonylation reaction leading to 1-aryl-3,3-diphenylprop-2-en-1-ones 6b-h has been established to proceed through a one-photon two-bond cleavage mechanism.[28,29] As evident from the ϕ_p data compiled in Table III.2, the cyano and phenyl groups as p-substituents on C-5 aryl group significantly lower the efficiency of this reaction. From the onsets of the lowest-energy band systems of 5a-h, no significant variation is noted in their singlet energy ($E_S \sim$ 89 kcal mol^{-1} from the onsets of fluorescence spectra of 5g and 5h in

methanol). The quantum yields of fluorescence and inter-
system crossing are small for these systems. Thus, the
smaller value of Φ_p in the case of 5g and 5h must be due to
the availability of nonradiative processes from the singlet
states of these systems.

III.4 EXPERIMENTAL SECTION

All melting points are uncorrected and were determined
on a Mel-Temp apparatus. The IR spectra were recorded on a
Perkin-Elmer Model 377 infrared spectrometer and the UV
spectra on Cary 17D or Cary 219 spectrometers. The ^{1}H NMR
spectra were recorded on a Varian EM-390 spectrometer, using
tetramethylsilane as internal standard. The mass spectra
were recorded on a JEOL JMS-D 300 mass spectrometer. All
steady-state irradiation experiments were carried out in a
Sreenivasan-Griffin-Rayonet photochemical reactor (RPR 300 nm
light source for direct and 350 nm light source for sensitized
irradiation experiments).

III.4.1 Starting Materials. The 1-aryl-3,4-diphenylbut-
2-en-1,4-diones, 10b,[39] mp 157-158 °C, 10c,[40] mp 116-117 °C,
10d,[39] mp 176-177 °C, 10e,[41] mp 155-156 °C, 10f,[39] mp 182-
183 °C, 10g,[42] mp 200-201 °C and 10h,[40] mp 131-132 °C and
3,3,5-triphenyl-2(3H)-furanone (5a),[1,2] mp 120-121 °C were

prepared by reported procedures. Solvents for steady-state irradiation experiments were purified and distilled before use. Aldrich Gold-Label solvents were used for laser studies. Petroleum ether used was the fraction with bp 60-80 °C.

III.4.2 <u>Preparation of 5-Aryl-3,3-diphenyl-2(3H)-furanones <u>5b-h</u></u>. A general procedure[1,2] adopted for the preparation of <u>5b-h</u> involved the neat heating of the appropriate 1-aryl-3,4-diphenylbut-2-en-1,4-diones <u>10b-h</u>, in glass tubes sealed under nitrogen, at 270-280 °C for 1/2-3/4 h. The thermolysate, after cooling, was chromatographed over silica gel. The product thus obtained was purified, in each case, by recrystallization from a mixture (1:3) of chloroform and ethanol.

<u>3,3-Diphenyl-5-(4-methylphenyl)-2(3H)-furanone</u> (<u>5b</u>).
<u>5b</u> was obtained in a 89% yield, mp 152-153 °C (lit.[43] mp 152-152.5 °C).

<u>3,3-Diphenyl-5-(4-ethylphenyl)-2(3H)-furanone</u> (<u>5c</u>). <u>5c</u> was obtained in a 63% yield, mp 92-93 °C.

IR spectrum ν_{max} (KBr): 3070, 3040, 3010, 2960, 2920, 2860 (CH), 1780 (C=O), 1630 and 1590 (C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 218 nm (ε, 29,500, sh), 243 (18,500, sh), 265 (23,300, sh), 273 (23,900), and 295 (8100).

^{1}H NMR spectrum (CDCl$_3$): δ 1.25 (3 H, t, J = 7.5 Hz, CH$_3$), 2.67 (2 H, q, J = 7.5 Hz, CH$_2$), 6.30 (1 H, s, vinylic), and 7.50 (14 H, m, aromatic).

Anal. Calcd for C$_{24}$H$_{20}$O$_2$: C, 84.71; H, 5.88. Found: C, 84.84; H, 6.02.

3,3-Diphenyl-5-(4-methoxyphenyl)-2(3H)-furanone (5d). 5d was isolated in a 89% yield, mp 170-171 °C (lit.[44] mp 171 °C).

3,3-Diphenyl-5-(4-ethoxyphenyl)-2(3H)-furanone (5e). 5e was isolated in a 79% yield, mp 95-96 °C.

IR spectrum ν_{max} (KBr): 3080, 3040, 2960, 2900, 2860 (CH), 1770 (C=O), 1630 and 1600 (C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 222 nm (ε, 19,600, sh), 247 (10,400, sh), 267 (17,400, sh), 281 (22,700), and 306 (6500, sh).

^{1}H NMR spectrum (CDCl$_3$): δ 1.50 (3 H, t, J = 7.5 Hz, CH$_3$), 4.20 (2 H, q, J = 7.5 Hz, CH$_2$), 6.30 (1 H, s, vinylic), and 7.50 (14 H, m, aromatic).

Anal. Calcd for C$_{24}$H$_{20}$O$_3$: C, 80.90; H, 5.62. Found: C, 80.68; H, 5.81.

5-(4-Chlorophenyl)-3,3-diphenyl-2(3H)-furanone (5f).[45] 5f was obtained in a 76% yield, mp 173-174 °C.

IR spectrum ν_{max} (KBr): 3100, 3040, 3020 (CH), 1770 (C=O), 1635 and 1580 (C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 214 nm (ε, 26,900, sh), 222 (21,700, sh), 261 (15,200, sh), 268 (17,800, sh), 275 (18,900), and 299 (4600, sh).

^{1}H NMR spectrum (CDCl$_3$): δ 6.30 (1 H, s, vinylic) and 7.50 (14 H, m, aromatic).

<u>Anal</u>. Calcd for C$_{22}$H$_{15}$ClO$_2$: C, 76.30; H, 4.34. Found: C, 76.43; H, 4.42.

<u>5-(4-Cyanophenyl)-3,3-diphenyl-2(3H)-furanone</u> (<u>5g</u>). <u>5g</u> was obtained in a 78% yield, mp 188-189 ^{o}C.

IR spectrum ν_{max} (KBr): 3080, 3050, 3010 (CH), 2220 (C≡N), 1790 (C=O), 1650 and 1600 (C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 220 nm (ε, 28,700, sh), 263 (13,200), 268 (15,900), and 286 (24,600).

^{1}H NMR spectrum (CDCl$_3$): δ 6.50 (1 H, s, vinylic) and 7.55 (14 H, m, aromatic).

<u>Anal</u>. Calcd for C$_{23}$H$_{15}$NO$_2$: C, 81.90; H, 4.45; N, 4.15. Found: C, 82.05; H, 4.50; N, 3.95.

<u>5-(4-Biphenylyl)-3,3-diphenyl-2(3H)-furanone</u> (<u>5h</u>). <u>5h</u> was isolated in a 77% yield, mp 193-194 ^{o}C (lit.[46] mp 195 ^{o}C).

II.4.3 Irradiation of 3,3,5-Triphenyl-2(3H)-furanone

(5a).[26-29]   A solution of 5a (320 mg, 1 mmol) and p-methoxy-acetophenone (150 mg, 1 mmol) in benzene (200 mL) was irradiated for 2 h. Removal of the solvent under vacuum gave a residual solid, which was triturated with chloroform. The solid material was filtered and washed with chloroform to give 30 mg (9%) of 11a, mp >360 °C.

IR spectrum ν_{max} (KBr): 3060, 3020, 2920 (CH), and 1765 (C=O) cm^{-1}.

Anal. Calcd for $C_{44}H_{32}O_4$: C, 84.62; H, 5.13. Found: C, 84.48; H, 5.27.

After the removal of chloroform from the filtrate, the residual solid was chromatographed over silica gel. Elution with a mixture (1:4) of benzene and petroleum ether gave 75 mg (23%) of the unchanged 5a, mp 120-121 °C (mixture melting point). Further elution with a mixture (1:1) of benzene and petroleum ether gave 30 mg (9%) of the phenanthrofuranone 9a, mp 259-261 °C (mixture melting point). Subsequent elution with a mixture (7:3) of benzene and petroleum ether gave 155 mg (48%) of the 2(5H)-furanone 7a, mp 124-125 °C (mixture melting point).

III.4.4 <u>Irradiation of 3,3-Diphenyl-(4-methylphenyl)-2(3H)-furanone</u> (<u>5b</u>). A solution of <u>5b</u> (165 mg, 0.5 mmol) in benzene (100 mL) was irradiated for 6 h. Removal of the solvent under vacuum gave a residual solid, which was recrystallized from ethanol to give 140 mg (93%) of <u>6b</u>, mp 92-93 °C[47] (mixture melting point). In a repeat run, a solution of <u>5b</u> (165 mg, 0.5 mmol) and piperylene (135 mg, 2 mmol) in benzene (100 mL) was irradiated for 6 h and workup as in the earlier case gave 142 mg (95%) of <u>6b</u>, mp 92-93 °C (mixture melting point).

In a separate experiment, a benzene solution of <u>5b</u> (325 mg, 1 mmol in 200 mL) was irradiated in the presence of <u>p</u>-methoxyacetophenone (150 mg, 1 mmol) for 2 h. The solvent was removed under reduced pressure and the resultant solid was triturated with chloroform to give 40 mg (12%) of <u>11b</u>, mp >360 °C.

IR spectrum ν_{max} (KBr): 3020, 2960, 2920 (CH), and 1760 (C=O) cm^{-1}.

Mass spectrum, m/e (relative intensity): 652 (M^+, 1), 326 ($M^+/2$, 100), 207 (48), 178 (73), 119 ($CH_3C_6H_4CO^+$, 80), and other peaks.

<u>Anal</u>. Calcd for $C_{46}H_{36}O_4$: C, 84.66; H, 5.52. Found: C, 84.60; H, 5.12.

The residual solid, after the removal of solvent from the chloroform layer, was chromatographed over silica gel. Elution with a mixture (1:4) of benzene and petroleum ether gave 75 mg (23%) of the unchanged 5b, mp 152-153 °C (mixture melting point). Further elution with a mixture (1:1) of benzene and petroleum ether gave 58 mg (18%) of the phenanthrofuranone 9b, mp 254-255 °C, after recrystallization from a mixture (1:1) of chloroform and ethanol.

IR spectrum ν_{max} (KBr): 3040, 3020, 2960, 2910 (CH), and 1750 (C=O) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 229 nm (ε, 28,600), 250 (28,400, sh), 256 (29,500), 274 (8400), 300 (6900), and 311 (5700, sh).

^{1}H NMR spectrum (CDCl$_3$): δ 2.35 (3 H, s, CH$_3$), 6.70 (1 H, s, CH), 7.60 (10 H, m, aromatic), 8.80 and 9.30 (2 H, m, H-7 and H-8).

Mass spectrum, m/e (relative intensity): 324 (M$^+$, 36), 295 (M$^+$ - CO, - H, 12), 205 (M$^+$ - CO, - CH$_3$C$_6$H$_4$, 100), 176 (28), 119 (CH$_3$C$_6$H$_4$CO$^+$, 22), and other peaks.

Anal. Calcd for C$_{23}$H$_{16}$O$_2$: C, 85.19; H, 4.94. Found: C, 85.31; H, 5.01.

Subsequent elution of the silica gel column with a mixture (7:3) of benzene and petroleum ether gave 130 mg

(40%) of the 2(5H)-furanone **7b**, mp 119-120 °C[23] (mixture melting point), after recrystallization from ethanol.

In a repeat run, a solution of **5b**, (325 mg, 1 mmol) and p-methoxyacetophenone (150 mg, 1 mmol) in hexane (200 mL) was irradiated for 2 h. Workup of the photolysate as in the earlier cases gave a mixture of **9b** (68 mg, 11%), mp 254-255 °C (mixture melting point), **11b** (228 mg, 70%), mp >360 °C and the unchanged **5b** (10 mg, 3%), mp 152-153 °C (mixture melting point).

In a separate experiment, a solution of **5b** (325 mg, 1 mmol) and p-methoxyacetophenone (150 mg, 1 mmol) in acetonitrile (200 mL) was irradiated for 2 h and worked up as in the earlier cases to give 75 mg (23%) of **7b**, mp 119-120 °C (mixture melting point), 100 mg (31%) of **9b**, mp 254-255 °C (mixture melting point) and 95 mg (29%) of the unchanged **5b**, mp 152-153 °C (mixture melting point).

In yet another experiment, a solution of **5b** (325 mg, 1 mmol) and p-methoxyacetophenone (150 mg, 1 mmol) in methanol (200 mL) was irradiated for 4 h. Workup of the photolysate by removal of the solvent under reduced pressure and recrystallization of the residue from a mixture (1:4) of benzene and petroleum ether gave 300 mg (83%) of **16b**, mp 126-127 °C.

IR spectrum ν_{max} (KBr): 3060, 3030, 2990, 2960, 2940, 2920 (CH), 1775 (C=O), and 1600 (C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 226 nm (ε, 29,300, sh), 238 (18,600, sh), and 273 (1900).

^{1}H NMR spectrum (CDCl$_3$): δ 2.20 (3 H, s, CH$_3$), 3.20 (3 H, s, OCH$_3$), 4.25 (1 H, d, J = 8 Hz, CH), 5.00 (1 H, d, J = 8 Hz, CH), and 7.05 (14 H, m, aromatic).

Anal. Calcd for C$_{24}$H$_{22}$O$_3$: C, 80.45; H, 6.15. Found: C, 80.81; H, 6.23.

In a repeat run, a solution of 5b (325 mg, 1 mmol) and p-methoxyacetophenone (150 mg, 1 mmol) in a mixture (9:1) of benzene and methanol was irradiated for 4 h. Workup as in the earlier case gave 310 mg (86%) of 16b, mp 126-127 °C (mixture melting point).

Irradiation of 3,4-Diphenyl-5-(4-methylphenyl)-2(5H)-furanone (7b). A benzene solution of 7b (65 mg, 0.2 mmol in 50 mL) was irradiated for 4 h (RPR, 300 nm). Removal of the solvent under reduced pressure gave a residue, which was recrystallized from a mixture (1:1) of chloroform and ethanol to give 58 mg (90%) of 9b, mp 254-255 °C (mixture melting point).

III.4.5 Irradiation of 3,3-Diphenyl-5-(4-ethylphenyl)-2(3H)-furanone (5c). A solution of 5c (170 mg, 0.5 mmol)

in benzene (100 mL) was irradiated for 6 h. Removal of the solvent under vacuum gave a residue, which was recrystallized from ethanol to give 145 mg (94%) of 6c, mp 96-97 °C.

IR spectrum ν_{max} (KBr): 3050, 3020, 2990 (CH), 1635 (C=O), 1600 and 1570 (C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 228 nm (ε, 14,100), 270 (12,200), 293 (11,300), and 310 (10,700, sh).

^{1}H NMR spectrum (CDCl$_3$): δ 1.30 (3 H, t, J = 7.5 Hz, CH$_3$), 2.75 (2 H, q, J = 7.5 Hz, CH$_2$), and 7.60 (15 H, m, aromatic and vinylic).

Anal. Calcd for C$_{23}$H$_{20}$O: C, 88.46; H, 6.41. Found: C, 88.68; H, 6.13.

In a repeat experiment, a solution of 5c (340 mg, 1 mmol) and p-methoxyacetophenone (150 mg, 1 mmol) in benzene (200 mL) was irradiated for 2 h. The solvent was removed under reduced pressure and the residual solid was triturated with chloroform to give 58 mg (17%) of the dimer 11c, mp >360 °C.

IR spectrum ν_{max} (KBr): 3060, 3030, 2970, 2920 (CH), and 1770 (C=O) cm^{-1}.

Mass spectrum, m/e (relative intensity): 679 (M$^+$ - H, 2), 340 (M$^+$/2, 100), 235 (16), 206 (41), 178 (60), 133 (C$_2$H$_5$C$_6$H$_4$CO$^+$, 73), and other peaks.

Anal. Calcd for $C_{48}H_{40}O_4$: C, 84.71; H, 5.88. Found: C, 84.84; H, 6.02.

The residual solid, after the removal of the solvent from the chloroform layer was chromatographed over silica gel. Elution with a mixture (1:4) of benzene and petroleum ether gave 57 mg (17%) of the unchanged 5c, mp 92-93 °C (mixture melting point). Further elution with a mixture (1:1) of benzene and petroleum ether gave 150 mg (44%) of the phenanthrofuranone 9c, mp 225-226 °C, after recrystallization from a mixture (1:3) of chloroform and ethanol.

IR spectrum ν_{max} (KBr): 3040, 3020, 2960, 2930 (CH), and 1745 (C=O) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 230 nm (ε, 32,400), 253 (31,700, sh), 259 (32,900), 275 (9200), 301 (7700), and 313 (7100, sh).

^{1}H NMR spectrum (CDCl$_3$): δ 1.20 (3 H, t, J = 7.5 Hz, CH$_3$), 2.67 (2 H, q, J = 7.5 Hz, CH$_2$), 6.67 (1 H, s, CH), 7.50 (10 H, m, aromatic), 8.80 and 9.25 (2 H, m, H-7 and H-8).

Mass spectrum, m/e (relative intensity): 338 (M$^+$, 69), 309 (M$^+$ - H, - CO, 23), 205 (M$^+$ - CO, - C$_2$H$_5$C$_6$H$_4$, 100), 177 (54), 133 (C$_2$H$_5$C$_6$H$_4$CO$^+$, 45), and other peaks.

Anal. Calcd for $C_{24}H_{18}O_2$: C, 85.20; H, 5.32. Found: C, 5.32; H, 5.14.

III.4.6 <u>Irradiation of 3,3-Diphenyl-5-(4-methoxyphenyl)-2(3H)-furanone</u> (<u>5d</u>). A benzene solution of <u>5d</u> (170 mg, 0.5 mmol in 100 mL) was irradiated for 6 h. Removal of the solvent under vacuum, followed by recrystallization of the residue from ethanol gave 150 mg (96%) of <u>6d</u>, mp 101-102 $^\circ$C.[48]

IR spectrum ν_{max} (KBr): 3030, 2980, 2950 (CH), 1640 (C=O), and 1595 (C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 229 nm (ε, 19,800) and 305 (16,900).

^{1}H NMR spectrum (CDCl$_3$): δ 3.85 (3 H, s, OCH$_3$) and 7.40 (15 H, m, aromatic and vinylic).

<u>Anal</u>. Calcd for C$_{22}$H$_{18}$O$_2$: C, 84.07; H, 5.73. Found: C, 84.35; H, 5.47.

In a separate experiment, a solution of <u>5d</u> (345 mg, 1 mmol) and <u>p</u>-methoxyacetophenone (150 mg, 1 mmol) in benzene (200 mL) was irradiated for 2 h. After removal of the solvent under reduced pressure, the residual solid was triturated with chloroform to give 120 mg (34%) of <u>11d</u>, mp >360 $^\circ$C.

IR spectrum ν_{max} (KBr): 3070, 3030, 2980, 2840 (CH), 1775 (C=O), 1610 and 1580 (C=C) cm^{-1}.

Mass spectrum, m/e (relative intensity): 342 (M$^+$/2, 60), 207 (12), 179 (26), 135 (CH$_3$OC$_6$H$_4$CO$^+$, 100), and other peaks.

The residual solid, after the removal of the solvent from the chloroform layer, was chromatographed over silica gel. Elution with a mixture (1:1) of benzene and petroleum ether gave 105 mg (30%) of the unchanged 5d, mp 170-171 °C (mixture melting point). Further elution with a mixture (7:3) of benzene and petroleum ether gave 30 mg (9%) of the phenanthrofuranone 9d, mp 238-239 °C, after recrystallization from a mixture (1:1) of benzene and petroleum ether.

IR spectrum ν_{max} (KBr): 3080, 3060, 2960 (CH), 1750 (C=O), and 1600 (C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 237 nm (ϵ, 31,800), 251 (27,600, sh), 257 (28,900), 276 (8000), 301 (6600), and 314 (5900, sh).

^{1}H NMR spectrum (CDCl$_3$): δ 3.80 (3 H, s, OCH$_3$), 6.67 (1 H, s, CH), 7.40 (10 H, m, aromatic), 8.80 and 9.35 (2 H, m, H-7 and H-8).

Mass spectrum, m/e (relative intensity): 340 (M$^+$, 52), 311 (M$^+$ - CO, - H, 14), 205 (M$^+$ - CO, - CH$_3$OC$_6$H$_4$, 100), 177 (33), 176 (35), 135 (CH$_3$OC$_6$H$_4$CO$^+$, 80), and other peaks.

Anal. Calcd for C$_{23}$H$_{16}$O$_3$: C, 81.18; H, 4.71. Found: C, 81.42; H, 4.93.

Subsequent elution with benzene gave 65 mg (19%) of the

2(5H)-furanone <u>7d</u>, mp 112-113 $^\circ$C^{23} (mixture melting point).

III.4.7 <u>Irradiation of 3,3-Diphenyl-5-(4-ethoxyphenyl)-2(3H)-furanone (5e)</u>. A solution of <u>5e</u> (180 mg, 0.5 mmol) in benzene (100 mL) was irradiated for 6 h. Removal of the solvent, followed by recrystallization of the residue from petroleum ether gave 155 mg (95%) of <u>6e</u>, mp 103-104 $^\circ$C.

IR spectrum ν_{max} (KBr): 3040, 3020, 2970, 2920 (CH), 1640 (C=O), 1590 and 1560 (C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 228 nm (ε, 18,700) and 304 (16,800).

^{1}H NMR spectrum (CDCl$_3$): δ 1.40 (3 H, t, J = 7.5 Hz, CH$_3$), 3.95 (2 H, q, J = 7.5 Hz, CH$_2$), and 7.30 (15 H, m, aromatic and vinylic).

<u>Anal</u>. Calcd for C$_{23}$H$_{20}$O$_2$: C, 84.15; H, 6.10. Found: C, 84.38; H, 5.95.

In a repeat run, a solution of <u>5e</u> (535 mg, 1 mmol) and p-methoxyacetophenone (150 mg, 1 mmol) in benzene (200 mL) was irradiated for 2 h. Removal of the solvent under vacuum, gave a residue, which was triturated with chloroform to give 215 mg (61%) of the dimer <u>11e</u>, mp >360 $^\circ$C.

IR spectrum ν_{max} (KBr): 3070, 3040, 2980, 2940, 2890, 2840 (CH), 1770 (C=O), 1610 and 1590 (C=C) cm^{-1}.

Mass spectrum, m/e (relative intensity): 711 (M^+ – H, 1), 356 ($M^+/2$, 84), 206 (10), 178 (22), 149 ($C_2H_5OC_6H_4CO^+$, 100), 121 ($C_2H_5OC_6H_4^+$, 28), and other peaks.

Anal. Calcd for $C_{48}H_{40}O_6$: C, 80.90; H, 5.62. Found: C, 80.71; H, 5.38.

The residue obtained from the chloroform washings, after removal of the solvent, was chromatographed over silica gel. Elution with a mixture (2:3) of benzene and petroleum ether gave 35 mg (10%) of the unchanged 5e, mp 95-96 °C (mixture melting point). Subsequent elution with a mixture (3:2) of benzene and petroleum ether gave 23 mg (6%) of 9e, mp 219-220 °C, after recrystallization from a mixture (1:4) of chloroform and ethanol.

IR spectrum ν_{max} (KBr): 3060, 3030, 2970, 2930 (CH), 1750 (C=O), and 1600 (C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 231 nm (ε, 28,400), 251 (23,900, sh), 257 (25,800), 275 (7900), 302 (5800), and 314 (5100, sh).

^{1}H NMR spectrum (CDCl$_3$): δ 1.40 (3 H, t, J = 7.5 Hz, CH$_3$), 4.03 (2 H, q, H = 7.5 Hz, CH$_2$), 6.63 (1 H, s, CH), 7.72 (10 H, m, aromatic), 8.80 and 9.25 (2 H, m, H-7 and H-8).

Mass spectrum, m/e (relative intensity): 354 (M^+, 73),

325 (M^+ – CO, – H, 17), 205 (M^+ – CO, – $C_2H_5OC_6H_4$, 100), 176 (33), 149 ($C_2H_5OC_6H_4CO^+$, 100), and other peaks.

Anal. Calcd for $C_{24}H_{18}O_3$: C, 81.36; H, 5.08. Found: C, 81.30; H, 5.00.

Further elution with benzene gave 43 mg (12%) of 7e, isolated as a waxy material which could not be crystallized.

IR spectrum ν_{max} (neat): 3060, 2980, 2930 (CH), 1745 (C=O), and 1600 (C=C) cm^{-1}.

^{1}H NMR spectrum (CDCl$_3$): δ 1.66 (3 H, t, J = 7.5 Hz, CH$_3$), 3.95 (2 H, q, J = 7.5 Hz, CH$_2$), 6.20 (1 H, s, CH), and 7.25 (14 H, m, aromatic).

Irradiation of 3,4-Diphenyl-5-(4-ethoxyphenyl)-2(5H)-fu-ranone (7e). A solution of 7e (70 mg, 0.2 mmol) in benzene (50 mL) was irradiated for 4 h (RPR, 300 nm). Removal of the solvent, followed by recrystallization of the residue from a mixture (1:4) of chloroform and ethanol gave 60 mg (89%) of 9e, mp 219-220 °C (mixture melting point).

III.4.8 Irradiation of 5-(4-Chlorophenyl)-3,3-diphenyl-2(3H)-furanone (5f). Irradiation of a benzene solution of 5f (175 mg, 0.5 mmol in 100 mL) for 6 h, followed by workup in the usual manner gave 150 mg (94%) of 6f, mp 100-101 °C, after recrystallization from ethanol.

IR spectrum ν_{max} (KBr): 3060, 3040 (CH), 1650 (C=O), 1590 and 1580 (C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 231 nm (ε, 15,600, sh), 264 (14,300), 291 (11,100, sh), and 311 (11,000).

^{1}H NMR spectrum (CDCl$_3$): δ 7.53 (m, aromatic and vinylic).

Anal. Calcd for C$_{21}$H$_{15}$ClO: C, 79.25; H, 4.72. Found: C, 79.61; H, 4.51.

In a separate experiment, a solution of 5f (350 mg, 1 mmol) and p-methoxyacetophenone (150 mg, 1 mmol) in benzene (200 mL) was irradiated for 2 h. Removal of the solvent under vacuum gave a residual solid, which was triturated with chloroform to give 30 mg (9%) of 11f, mp >360 ^{o}C.

IR spectrum ν_{max} (KBr): 3050, 3020 (CH), and 1765 (C=O) cm^{-1}.

Mass spectrum, m/e (relative intensity): 691 (M$^+$ - H, 1), 346 (M$^+$/2, 80), 207 (68), 179 (100), 139 (ClC$_6$H$_4$CO$^+$, 23), and other peaks.

Anal. Calcd for C$_{44}$H$_{30}$Cl$_2$O$_4$: C, 76.30; H, 4.34. Found: C, 76.56; H, 4.21.

The residual solid, after the removal of the solvent from the chloroform layer, was chromatographed over silica gel.

Elution with a mixture (1:4) of benzene and petroleum ether gave 95 mg (29%) of the unchanged 5f, mp 173-174 $^{\circ}$C (mixture melting point). Further elution with a mixture (1:1) of benzene and petroleum ether gave 55 mg (16%) of the phenanthrofuranone 9f, mp 255-256 $^{\circ}$C, after recrystallization from a mixture (1:1) of chloroform and ethanol.

IR spectrum ν_{max} (KBr): 3060, 3020 (CH), and 1750 (C=O) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 236 nm (ε, 22,100), 251 (20,600, sh), 257 (22,000), 301 (5100), and 314 (4500, sh).

^{1}H NMR spectrum (CDCl$_3$): δ 6.67 (1 H, s, CH), 7.55 (10 H, m, aromatic), 8.80 and 9.25 (2 H, m, H-7 and H-8).

Mass spectrum, m/e (relative intensity): 344 (M$^+$, 22), 315 (M$^+$ - CO, - H, 5), 265 (11), 205 (M$^+$ - CO, - ClC$_6$H$_4$, 100), 139 (ClC$_6$H$_4$CO$^+$, 5), and other peaks.

Anal. Calcd for C$_{22}$H$_{13}$ClO$_2$: C, 76.74; H, 3.78. Found: C, 77.06; H, 3.90.

Subsequent elution of the silica gel column with a mixture (7:3) of benzene and petroleum ether gave 135 mg (39%) of the 2(5H)-furanone 7f, mp 132-133 $^{\circ}$C, after recrystallization from ethanol.

IR spectrum ν_{max} (KBr): 3020 (CH), 1750 (C=O), and 1570 (C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 232 nm (ε, 46,600), 264 (25,900) and 277 (25,000, sh).

^{1}H NMR spectrum (CDCl$_3$): δ 6.33 (1 H, s, CH) and 7.40 (14 H, m, aromatic).

Mass spectrum, m/e (relative intensity): 346 (M$^+$, 24), 207 (M$^+$ - CO, - ClC$_6$H$_4$, 48), 179 (100), 178 (60), 139 (ClC$_6$H$_4$CO$^+$, 20), and other peaks.

<u>Anal</u>. Calcd for C$_{22}$H$_{15}$ClO$_2$: C, 76.30; H, 4.34. Found: C, 76.25; H, 3.98.

III.4.9 <u>Irradiation of 5-(4-Cyanophenyl)-3,3-diphenyl-2(3H)-furanone</u> (<u>5g</u>). A solution of <u>5g</u> (170 mg, 0.5 mmol) in benzene (100 mL) was irradiated for 6 h. Removal of the solvent under vacuum gave a product mixture, which was separated by preparative tlc over silica gel to give 10 mg (6%) of the unchanged <u>5g</u>, mp 188-189 $^\circ$C (mixture melting point) and 135 mg (87%) of <u>6g</u>, mp 141-142 $^\circ$C, after recrystallization from ethanol.

IR spectrum ν_{max} (KBr): 3050, 3020 (CH), 2220 (C≡N), 1650 (C=O), 1600 and 1570 (C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 247 nm (ε, 19,900), 254 (19,600, sh), 300 (9800), and 321 (9800).

^{1}H NMR spectrum (CDCl$_3$): δ 7.50 (m, aromatic and
vinylic).

Anal. Calcd for C$_{22}$H$_{15}$NO: C, 85.44; H, 4.85; N, 4.53.
Found: C, 85.11; H, 4.63; N, 4.51.

In a separate experiment, a solution of 5g (340 mg,
1 mmol) and p-methoxyacetophenone (150 mg, 1 mmol)in benzene
(200 mL) was irradiated for 2 h. The solvent was removed
under reduced pressure and the residual solid was chromatogra-
phed over silica gel. Elution with a mixture (1:1) of benzene
and petroleum ether gave 60 mg (18%) of the unchanged 5g,
mp 188-189 ^{o}C (mixture melting point). Further elution with
a mixture (7:3) of benzene and petroleum ether gave 35 mg
(10%) of 9g, mp 235-236 ^{o}C, after recrystallization from a
mixture (1:1) of chloroform and ethanol.

IR spectrum ν_{max} (KBr): 3060, 3040 (CH), 2440 (C≡N),
1750 (C=O), and 1610 (C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 231 nm (ε, 28,400), 251
(23,900, sh), 257 (25,800), 275 (8400), 301 (6800), and 313
(6200, sh).

^{1}H NMR spectrum (CDCl$_3$): δ 6.77 (1 H, s, CH), 7.35
(10 H, m, aromatic), 8.85 and 9.30 (2 H, m, H-7 and H-8).

Mass spectrum, m/e (relative intensity): 335 (M^+, 23), 306 (M^+ – CO, – H, 5), 291 (M^+ – CO_2, 5), 205 (M^+ – CO, – CNC_6H_4, 100), 176 (72), and other peaks.

<u>Anal</u>. Calcd for $C_{23}H_{13}NO_2$: C, 82.39; H, 3.88; N, 4.18. Found: C, 82.01; H, 4.13; N, 4.27.

Subsequent elution of the silica gel column with benzene gave 365 mg (52%) of the 2(5H)-furanone <u>7g</u>, mp 117–118 $^\circ$C[23] (mixture melting point), after recrystallization from ethanol.

In a repeat run, a solution of <u>5g</u> (340 mg, 1 mmol) and <u>p</u>-methoxyacetophenone (150 mg, 1 mmol) in methanol (200 mL) was irradiated for 5 h. The photolysate, after the removal of solvent, was chromatographed over silica gel. Elution with a mixture (1:1) of benzene and petroleum ether gave 70 mg (21%) of the unchanged <u>5g</u>, mp 188–189 $^\circ$C (mixture melting point). Further elution with a mixture (3:2) of benzene and petroleum ether gave 230 mg (62%) of <u>16g</u>, mp 152–153 $^\circ$C, after recrystallization from carbon tetrachloride.

IR spectrum ν_{max} (KBr): 3060, 3020, 3000, 2960, 2930, 2900 (CH), 2215 (C≡N), 1770 (C=O), and 1600 (C=C) cm^{-1}.

UV spectrum λ_{max} (CH_3OH): 244 nm (ϵ, 22,800), 254 (19,600, sh), 278 (2300), and 292 (2000).

^{1}H NMR spectrum (CDCl$_3$): δ 3.25 (3 H, s, OCH$_3$), 4.30
(1 H, d, J = 8 Hz, CH), 5.07 (1 H, d, J = 8 Hz, CH), and
7.20 (14 H, m, aromatic).

Anal. Calcd for C$_{24}$H$_{19}$NO$_3$: C, 78.05; H, 5.15; N, 3.79.
Found: C, 78.21; H, 5.01; N, 3.93.

III.4.10 Irradiation of 5-(4-Biphenylyl)-3,3-diphenyl-
2(3H)-furanone (5h). A benzene solution of 5h (195 mg,
0.5 mmol in 100 mL) was irradiated for 6 h. Removal of the sol-
vent, followed by recrystallization of the residue from
ethanol gave 165 mg (92%) of 6h, mp 121-122 $^\circ$C.

IR spectrum ν_{max} (KBr): 3040, 3020 (CH), 1645 (C=O),
and 1590 (C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 229 nm (ε, 20,600) and 307
(22,800).

^{1}H NMR spectrum (CDCl$_3$): δ 7.60 (m, aromatic and
vinylic).

Anal. Calcd for C$_{27}$H$_{20}$O: C, 90.00; H, 5.62. Found: C,
90.30; H, 5.84.

In a separate experiment, a solution of 5h and p-methoxy-
acetophenone (150 mg, 1 mmol) in benzene (200 mL) was irradia-
ted for 6 h. The solvent was removed under vacuum and the

residual solid was chromatographed over silica gel. Elution with a mixture (1:4) of benzene and petroleum ether gave 150 mg (38%) of the unchanged 5h, mp 193-194 °C (mixture melting point). Further elution with a mixture (1:1) of benzene and petroleum ether gave 155 mg (40%) of the phenan-throfuranone 9h, mp 284-286 °C, after recrystallization from chloroform.

IR spectrum ν_{max} (KBr): 3060, 3020 (CH), and 1750 (C=O) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 233 nm (ε, 28,300, sh), 252 (25,900, sh), 257 (26,600), 275 (8500), 301 (7000), and 315 (6000, sh).

^{1}H NMR spectrum (CDCl$_3$): δ 6.80 (1 H, s, CH), 7.65 (15 H, m, aromatic), 8.85 and 9.35 (2 H, m, H-7 and H-8).

Mass spectrum, m/e (relative intensity): 386 (M$^+$, 25), 357 (M$^+$ - CO, - H, 5), 340 (14), 205 (M$^+$ - CO, - C$_6$H$_5$C$_6$H$_4$, 100), 181 (C$_6$H$_5$C$_6$H$_4$CO$^+$, 18), and other peaks.

Anal. Calcd for C$_{28}$H$_{18}$O$_2$: C, 87.05; H, 4.66. Found: C, 86.63; H, 5.04.

Subsequent elution with a mixture (7:3) of benzene and petroleum ether gave 45 mg (12%) of the 2(5H)-furanone 7h, mp 169-170 °C, after recrystallization from ethanol.

IR spectrum ν_{max} (KBr): 3060, 3020 (CH), 1740 (C=O), and 1590 (C=C) cm^{-1}.

UV spectrum λ_{max} (CH$_3$OH): 245 nm (ε, 25,300) and 269 (22,200, sh).

^{1}H NMR spectrum (CDCl$_3$): δ 6.35 (1 H, s, CH) and 7.48 (19 H, m, aromatic).

Mass spectrum, m/e (relative intensity): 388 (M$^+$, 33), 360 (M$^+$ - CO, 27), 359 (M$^+$ - CO, - H, 40), 181 (C$_6$H$_4$C$_6$H$_5$CO$^+$, 78), 178 (100), and other peaks.

Anal. Calcd for C$_{28}$H$_{20}$O$_2$: C, 86.60; H, 5.15. Found: C, 86.75; H, 5.26.

III.4.11 Laser Flash Photolysis.[31] The computer-controlled set-up used for laser flash photolysis studies is described elsewhere.[49,50] The pulsed laser sources were: Lambda-Physik EMG 101 MSC excimer (308 nm, ~20 ns), Molectron UV-400 nitrogen (337.1 nm, ~8 ns) and Quanta-Ray DCR-1 Nd-YAG (third harmonic, 355 nm, ~6 ns). Deoxygenation of solutions was effected by saturation with argon.

III.5 REFERENCES

(1) F. R. Japp and F. Klingemann, J. Chem. Soc., 57, 662 (1890).

(2) A. H. Blatt, J. Org. Chem., 15, 869 (1950).

(3) K. B. Wiberg and T. W. Hutton, J. Am. Chem. Soc., 76, 5367 (1954).

(4) A. Yogev and Y. Mazur, J. Am. Chem. Soc., 87, 3520 (1965).

(5) C. D. Gutsche and B. A. M. Oude-Alink, J. Am. Chem. Soc., 90, 5855 (1968).

(6) I. S. Krull and D. R. Arnold, Tetrahedron Lett., 1247 (1969).

(7) G. Rio and J. -C. Hardy, Bull. Soc. Chim. Fr., 3572 (1970).

(8) G. Rio and J. -C. Hardy, Bull. Soc. Chim. Fr., 3578 (1970).

(9) O. L. Chapman and C. L. McIntosh, J. Chem. Soc., Chem. Commun., 383 (1971).

(10) B. A. M. Oude-Alink, A. W. K. Chan and C. D. Gutsche, J. Org. Chem., 38, 1993 (1973).

(11) A. Padwa and G. A. Lee, J. Am. Chem. Soc., 95, 6147 (1973).

(12) A. Padwa and A. Au, J. Am. Chem. Soc., 96, 1633 (1974).

(13) A. Padwa and G. A. Lee, J. Am. Chem. Soc., 96, 1634
(1974).

(14) K. Ohga and T. Matsuo, J. Org. Chem., 39, 106 (1974).

(15) A. Padwa, D. Dehm, T. Oine and G. A. Lee, J. Am. Chem.
Soc., 97, 1837 (1975).

(16) A. Padwa and D. Dehm, J. Am. Chem. Soc., 97, 4779
(1975).

(17) W. Skorianetz and G. Ohloff, Helv. Chim. Acta, 58,
1272 (1975).

(18) Y. S. Rao, Chem. Rev., 76, 625 (1976).

(19) Y. Kosugi, S. Sekiguchi, R. Sekita and H. Uda, Bull.
Chem. Soc. Jpn., 49, 520 (1976).

(20) K. Ohga and T. Matsuo, Bull. Chem. Soc. Jpn., 49,
1590 (1976).

(21) A. Padwa, A. Ku and E. Sato, Tetrahedron Lett., 2409
(1976).

(22) A. Padwa, T. Brookhart, D. Dehm, G. West and G.
Wubbels, J. Am. Chem. Soc., 99, 2347 (1977).

(23) A. Padwa, T. Brookhart, D. Dehm and G. Wubbels,
J. Am. Chem. Soc., 100, 8247 (1978).

(24) H. Zimmer and B. W. Downs, Heterocycl. Chem., 15,
703 (1978).

(25) R. M. Utrilla and M. A. Miranda, Tetrahedron, 37, 2111 (1981).

(26) B. B. Lohray, Ph. D. Thesis, Indian Institute of Technology, Kanpur, India (1983).

(27) B. B. Lohray, C. V. Kumar, P. K. Das and M. V. George, J. Am. Chem. Soc., 106, 7352 (1984).

(28) K. R. Gopidas, Ph. D. Thesis, Indian Institute of Technology, Kanpur, India (1987).

(29) K. R. Gopidas, B. B. Lohray, S. Rajadurai, P. K. Das and M. V. George, J. Org. Chem., 52, 2831 (1987).

(30) H. F. Davis, B. B. Lohray, K. R. Gopidas, C. V. Kumar, P. K. Das and M. V. George, J. Org. Chem., 50, 3865 (1985).

(31) All laser flash photolysis studies have been carried out by Dr. P. K. Das, Mr. D. R. Cyr and Professor M. V. George at the Radiation Laboratory, University of Notre Dame (U. S. A.).

(32) S. L. Murov, "Handbook of Photochemistry", Marcel Dekker, New York (1973).

(33) R. Bensasson and J. -C. Gramain, J. Chem. Soc., Faraday Trans. 1, 76, 1801 (1980).

(34) R. Bensasson and E. J. Land, Photochem. Photobiol. Rev., 3, 163 (1978).

(46) W. Ried and H. Mengler, Ger., 1, 189, 987
(Cl. C 07 C) (1965); Chem. Abstr., 62, 16146e (1965).

(47) J. Robin, Ann. Chim., 16, 421 (1931).

(48) R. N. Iyer and R. Gopalchari, Indian J. Pharm., 31, 49 (1969).

(49) P. K. Das, M. V. Encinas, R. D. Small, Jr. and J. C. Scaiano, J. Am. Chem. Soc., 101, 6965 (1979) and references therein.

(50) V. Nagarajan and R. W. Fessenden, J. Phys. Chem., 89, 2330 (1985).

VITAE

Born on May 30, 1958, at Vazhakkulam (Kerala),
S. Prathapan completed his schooling in 1973. He obtained
the degree of Bachelor of Science from Newman College,
Thodupuzha, University of Kerala in 1978 and the degree
of Master of Science from the Department of Applied
Chemistry, University of Cochin, Kalamassery in 1981.

He joined the Ph.D. programme in the Department of
Chemistry, Indian Institute of Technology, Kanpur in
December 1981. Presently, he is a Senior Research Fellow
in the same department.